Characterization of Organic Contaminants in Ash Samples from Pulverized Coal-Fired Power Generating Stations

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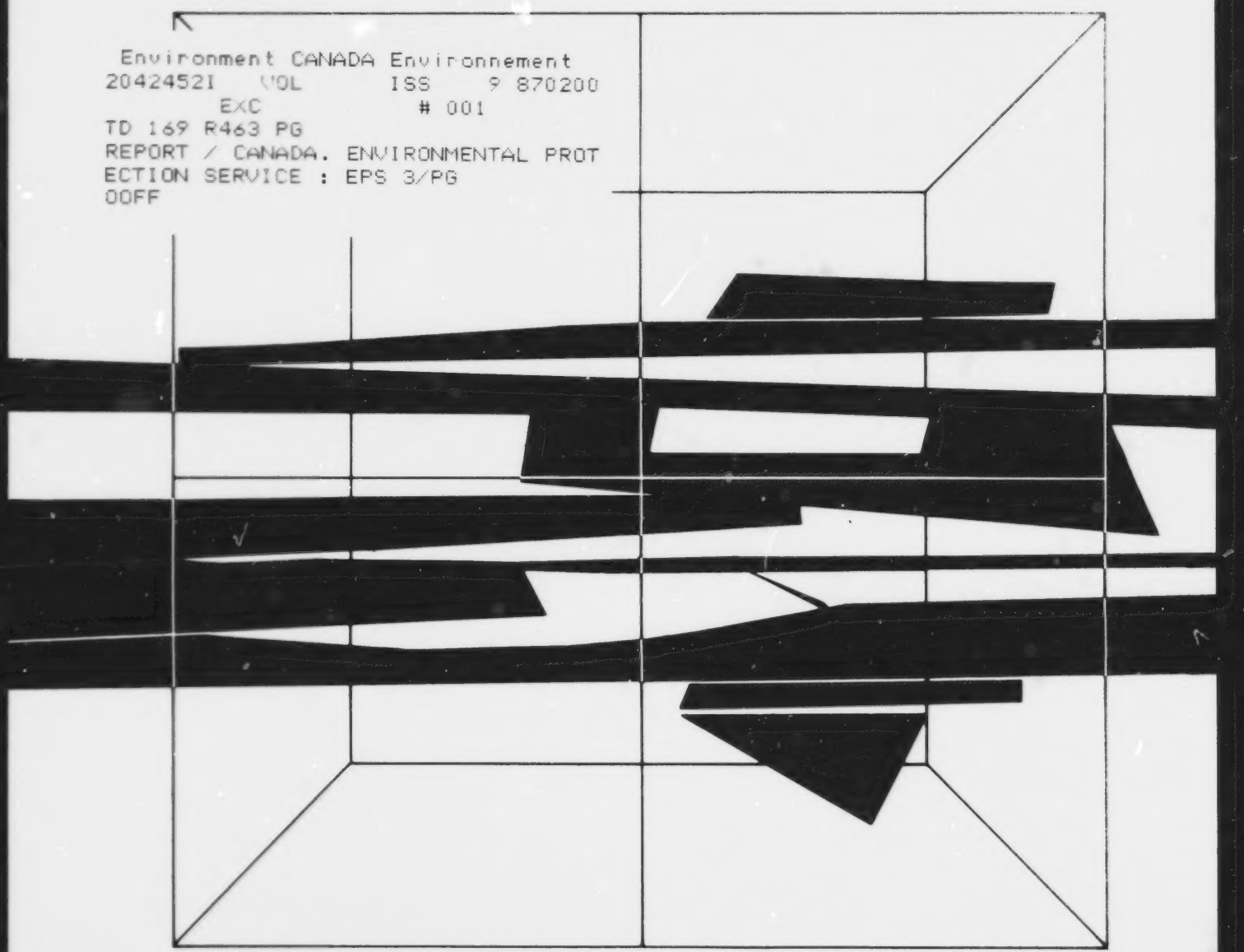

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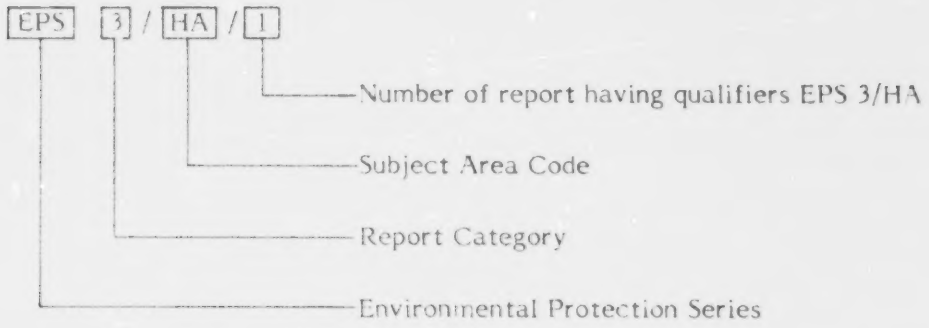

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CHARACTERIZATION OF ORGANIC CONTAMINANTS IN ASH SAMPLES FROM PULVERIZED COAL-FIRED POWER GENERATING STATIONS

by

Zenon Environmental Inc.

for the

Industrial Programs Branch
Environmental Protection
Conservation and Protection
Environment Canada

Report EPS 3/PG/9
February 1987

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EXECUTIVE SUMMARY

This study consists of two parts, Sections A and B. In Section A, the ashes of several coal-fuelled power generating stations were analyzed for

- contaminant identification
- quantitation of polyaromatic hydrocarbons (PAH)
- quantitation of polychlorinated dibenzofurans (PCDF) and dibenzo-p-dioxins (PCDD).

The full-scan GC/MS characterization and comparison of methods of analysis on ash samples revealed that the indicated presence of a broad array of benzyl compounds is an artifact of the toluene extraction process. Comparison of benzene soxhlet and toluene soxhlet extraction techniques revealed that while toluene provided higher extraction efficiency of several PAH, the artifacts produced limited the analysis of lower concentrations of ash contaminants.

The analysis of polyaromatic hydrocarbons in 23 PCF fly ash samples revealed low or no detectable concentrations of PAH in all samples. These samples contained predominantly phenanthrene, fluoranthene, pyrene, and naphthalene. These results are similar to previous ones.

The quality control data on the surrogate standard showed an average recovery from all samples of 49 $\pm$ 26 percent, which compares well with other reports. In addition, good agreement was obtained in this study with the certified values on samples of the NBS reference material of urban dust.

Analysis of the 23 ash samples for polychlorinated dibenzo-p-dioxins and furans revealed generally very low levels of dibenzofurans (mainly the penta- and hexachloro homologues) and generally no detectable levels of polychlorinated dibenzo-p-dioxins. The concentrations of the dibenzofurans were higher for the pentachlorodibenzofurans than the concentrations of hexachlorodibenzofurans.

The quality control data indicated that the average recovery of labelled T_4CDD was 64 $\pm$ 34 percent, whereas the average recovery of labelled O_8CDD was 81 $\pm$ 39 percent. In addition, the standard reference material of urban dust was found to contain significant levels of PCDD and PCDF.

Total extractable organic halogen (TEOX) concentrations in PCF fly ashes were between <0.02 and 14.8 μg Cl/g.

TEOX concentrations appeared to correlate with the location of ash collection within the ESP banks but did not correlate well with PCDD/PCDF concentrations.

Quality control on TEOX produced an overall precision of ± 7.6 percent on TEOX analysis.

In Section B, the results of Section A and several previous studies of organic substances in coal ashes have been summarized and discussed. To date no extractable trace organics have been detected at concentrations above 0.5 μg/g in fly ashes captured by electrostatic precipitators on large pulverized coal-fired power generation stations. In general, the levels for the limited polychlorinated dibenzofurans and dioxins that have been detected in fly ashes from these power stations are several orders of magnitude lower than levels reported in municipal incinerator ashes. Other organics may be of greater interest for power station wastes.

RÉSUMÉ

La présente étude comporte deux parties, la section A et la section B. Dans la section A, on présente les résultats d'analyses des cendres de plusieurs centrales thermiques au charbon:

- identification des contaminants
- dosage des hydrocarbures polyaromatiques (HAP)
- dosage des dibenzofurannes et dibenzo-p-dioxines polychlorés (PCDF et PCDD).

La caractérisation détaillée CG/SM et la comparaison des méthodes analytiques utilisées pour les échantillons de cendres ont démontré que la présence indiquée de larges spectres de composés de type benzyle est due au processus d'extraction au toluène. La comparaison des techniques d'extraction Soxhlet au benzène et au toluène a montré que, alors que le toluène était plus efficace pour l'extraction de plusieurs HAP, la production de composés parasites limitait l'efficacité de l'analyse des faibles concentrations de contaminants des cendres.

L'analyse des hydrocarbures polyaromatiques dans 23 échantillons de cendres volantes PCF indiquait la présence de concentrations faibles ou non décelables de HAP dans tous les échantillons. Ces échantillons contenaient surtout du phénanthrène, du fluoranthène, du pyrène et du naphtalène. Ces résultats étaient semblables à ceux qui avaient déjà été obtenus.

Les données de contrôle de qualité obtenues avec un étalon simulé indiquaient une récupération moyenne de 49 $\pm$ 26 pour cent pour tous les échantillons, ce qui correspond assez bien avec les autres rapports. En outre, les résultats de la présente étude concordaient assez bien avec les valeurs certifiées d'échantillons de substances de référence NBS de poussière urbaine.

Le dosage des dibenzo-p-dioxines et des dibenzofurannes polychlorés indiquait généralement de très faibles teneurs en dibenzofuranne (principalement les homologues penta- et hexachloros) et, de façon générale, aucune teneur décelable en dibenzo-p-dioxines polychlorés. Dans le cas des dibenzofurannes, la concentration des pentachlorodibenzofurannes était supérieure à celle des hexachlorodibenzofurannes.

Les données de contrôle de qualité indiquaient que la récupération moyenne des T_4CDD étiquetés était de 64 $\pm$ 34 pour cent, alors qu'elle était de 81 $\pm$ 39 pour cent dans le cas des O_8CDD. De plus, on a constaté que la substance de référence standard

représentant la poussière urbaine contenait des teneurs significatives en PCDD et en PCDF.

Les concentrations totales de composés organiques halogénés extractibles (COHE) dans les cendres volantes PCF étaient comprises entre moins de 0,02 et 14,8 µg/Cl/g.

Les concentrations de COHE présentaient une certaine corrélation avec les données sur les emplacements de cueillette de cendres dans les banques ESP, mais la corrélation n'était pas aussi bonne pour ce qui est des concentrations de PCDD et de PCDF.

Les études de contrôle de la qualité des COHE indiquaient une précision de ± 7,6 pour cent pour les données analytiques.

Dans la section B, les résultats de la section A et ceux de plusieurs études antérieures de substances organiques trouvées dans les cendres de charbon ont été résumés et examinés. À ce jour, aucun produit organique extractible à l'état de traces n'a été décelé à des concentrations supérieures à 0,5 µg/g dans les cendres volantes capturées par des précipitateurs électrostatiques de grandes centrales thermiques au charbon pulvérisé. En général, les teneurs des espèces limitées de dibenzofurannes et de dioxines qui ont été décelées dans les cendres volantes provenant de ces centrales sont de plusieurs ordres de grandeur inférieures aux valeurs signalées dans les cendres des incinérateurs municipaux. Il se peut que l'étude d'autres composés organiques présente plus d'intérêt dans le cas des résidus des centrales thermiques.

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STUDY BACKGROUND

This study comprises two parts. The purpose of the first part (Section A) was to continue previous analytical work which focussed primarily on trace organics in ash samples produced in high-efficiency, pulverized coal-fired (PCF) power generating stations. Some analysis and discussion of bubbling atmospheric fluidized-bed combustion ashes were also included for reference.

The specific objectives were

i) to determine the levels of polyaromatic hydrocarbons, polychlorinated dibenzo-p-dioxins, and dibenzofurans in fly ash samples from conventional PCF power generating stations;

ii) to characterize other organic contaminants present in selected ashes and assess total extractable organic chlorine as a surrogate measurement parameter; and

iii) to compare benzene and toluene sample extraction procedures for PAH in ash samples.

The purpose of the second part of the study (Section B) was to compile and document the available information on trace organic contaminants in ashes from conventional PCF power generating stations including the results from the first part of this study, with particular emphasis on Canadian stations.

SECTION A

Characterization of Trace Organic Contaminants in Ashes from Pulverized Coal-Fired Power Generating Stations

1 INTRODUCTION

Emissions from coal-fired power generating stations have been an environmental concern since the mid-1960s. Researchers in the field focussed primarily on the presence of polyaromatic hydrocarbons (PAH) in stack gas, fly ash, and bed ash. (Hangebrauck et al., 1964, 1967; Diehl et al., 1966; Herman, 1974; and Bennett et al., 1979). With the reporting of polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) in ash samples and stack gas samples from municipal incinerators (Olie et al., 1977), concern shifted to the analysis of these compounds not only in the emissions of coal-fired power generating stations but also in refuse-derived fuel (RDF) and RDF-coal co-fired incinerators.

Lao et al. (Environment Canada, 1983) and Coburn et al. (Zenon, 1983) performed low-level PCDD/PCDF analyses on a variety of fly ash and bed ash samples from both pulverized coal-fired (PCF) and bubbling atmospheric fluidized-bed combustion (AFBC) units in Canadian coal-fired power generating stations. The Zenon study also provided a characterization of the other organics present and the quantitation of PAH in ash samples derived from different feed coals and different combustion conditions and technologies. In the United States, the Midwest Research Institute (Haile et al., 1983) performed a pilot study for the national assessment of specific organic compounds occurring in combustion processes. This study, performed on emissions from a municipal incinerator in Chicago and a RDF-coal co-fired incinerator in Ames, Iowa, focussed primarily on PCB, PAH, PCDD, and PCDF. The findings indicate that ashes produced in coal-fired power stations contain very low or non-detectable PCDD/PCDF residues, unlike ashes from municipal incinerators. PAH, however, have been consistently found in the ashes from coal-fired power stations in concentrations that vary with feed coal, combustion temperatures, residence time, and type of combustor. In addition, through full-scan gas chromatographic-mass spectrometric characterization, some ashes have been found to contain oxygen-containing PAH (Zenon, 1983). Researchers at Battelle (Wilson et al., 1983) concur; they tentatively identified oxygen-containing PAH and nitro-PAH, such as nitropyrene, in ash samples from PCF and bubbling AFBC units.

The recent focus on the analyses for PAH, PCDD, and PCDF may have deflected attention from other compounds in and the overall composition of ashes from coal combustion. Except for a study by Haile et al. (1983) at the Midwest Research Institute (MRI) in the U.S. and the Zenon study (Coburn et al., 1983) in Canada, very little has been reported on the characterization of other organic contaminants in fly ashes and

bed ashes from coal combustion units. The Zenon study identified a broad array of C-14 to C-21 benzyl derivatives, which may either be the products of the interaction of toluene, the extraction solvent, with the ash samples or the actual constitutents of these ash samples. Additional studies were recommended to assess this finding further.

In the MRI study, extraction methodologies were extensively tested for the recovery of fortified polyaromatic hydrocarbons. Their tests, which did not include toluene-soxhlet extraction, indicate that benzene-soxhlet extraction of a wet ash (1:2 water/ash) resulted in the recovery of the eight PAH - the highest recovery - from the fly ash tested. However, no extraction testing of naturally contaminated ashes was reported.

The MRI study also recommends that a good method for obtaining low-cost source data on combustion is the determination of total extractable organic halogens such as chlorine. This determination involved the analysis of a portion of the solvent extract through a microcoulometric cell for organic halogens, specifically organic chlorine and bromine.

This study uses the analysis of the solvent extract to provide additional data on selected ash samples from coal-fired power generating stations. The additional data for such target organics of concern as PAH, PCDD, and PCDF are to provide a more general characterization of trace organics by using different extraction procedures and to evaluate a low-cost indicator or surrogate parameter-total extractable organic halogen (TEOX), for example - as a possible source-monitoring technique.

2 SAMPLE DESCRIPTIONS

Two AFBC ash samples, one a bed ash and the other a fly ash from small bubbling units, were used for the comparison of extraction procedures for polyaromatic hydrocarbons (PAH).

Twenty-three ash samples collected from electrostatic precipitators (ESP) at the Poplar River, Battle River, and Lingan PCF power generating stations were analysed for PAH, polychlorinated dibenzo-p-dioxins (PCDD), and polychlorinated dibenzofurans (PCDF). The sample from the Poplar River PCF station was analyzed by full-scan gas chromatography-mass spectrometry.

The information about the samples and analyses is summarized in Table 2-1. Figures 2-1 to 2-3 show the layout of the ESP units at Poplar River, Battle River, and Lingan as well as the points of sample collection. These samples were collected by Battelle (Pacific Northwest Laboratories) during a study, "Environmental Implications of Trace Element Releases from Canadian Coal-Fired Generating Stations", for the Canadian Electrical Association and were provided for this study by the Environmental Protection Service of Environment Canada. Further details of these stations and their operation are included in the Battelle/CEA report.

TABLE 2-1 ASH ANALYSIS SCHEDULE

Station Location	Sample Identification	Analysis				
		Full Scan	TEOX	PAH	T_4CDD/F	PCDD/F
Poplar River, Alta.	PR-ESP3-85	x	x	x	x	x
Battle River, Sask.	BR-PFA3-2	-	x	x	x	x
	BR-PFA3-4	-	x	x	x	x
	BR-PFA3-6	-	x	x	x	x
	BR-PFA3-8	-	x	x	x	x
	BR-PFA3-10	-	x	x	x	x
	BR-PFA3-12	-	x	x	x	x
	BR-PFA3-14	-	x	x	x	x
	BR-PFA3-16	-	x	x	x	x
	BR-PFA4-2	-	x	x	x	x
	BR-PFA4-4	-	x	x	x	x
	BR-PFA4-6	-	x	x	x	x
	BR-PFA4-8	-	x	x	x	x
	BR-PFA4-10	-	x	x	x	x
	BR-PFA4-16	-	x	x	x	x
Lingan, N.S.	LNS-ESP1-15	-	x	x	x	x
	LNS-ESP1-11	-	x	x	x	x
	LNS-ESP1-7	-	x	x	x	x
	LNS-ESP1-4	-	x	x	x	x
	LNS-ESP1-2	-	x	x	x	x
	LNS-EPS2-11	-	x	x	x	x
	LNS-EPS2-4	-	x	x	x	x
	LNS-EPS2-2	-	x	x	x	x
Summerside, P.E.I. (AFBC)	Bed Ash	x	x	-	-	-
	Baghouse Ash	x	x	-	-	-

Note: x denotes that the analysis was carried out.

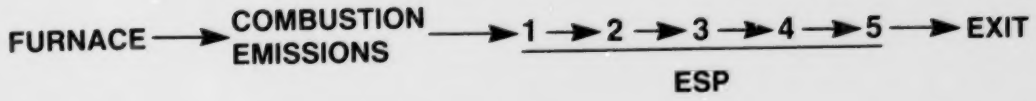

FIGURE 2-1 ARRANGEMENT OF ELECTROSTATIC PRECIPITATOR SAMPLING POINTS AT POPLAR RIVER GENERATING STATION

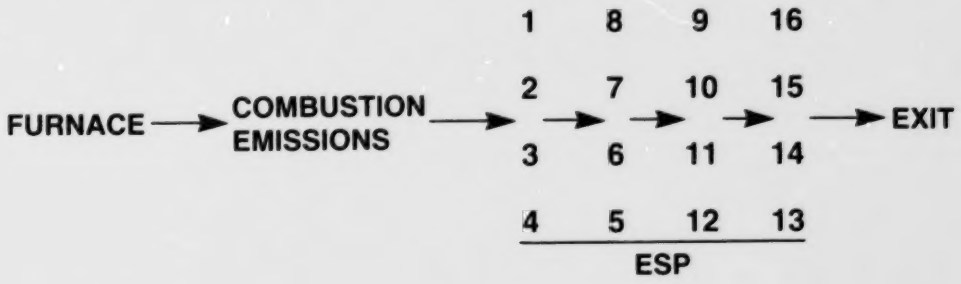

FIGURE 2-2(a) ARRANGEMENT OF ELECTROSTATIC PRECIPITATOR, ESP1, SAMPLING POINTS AT BATTLE RIVER GENERATING STATION

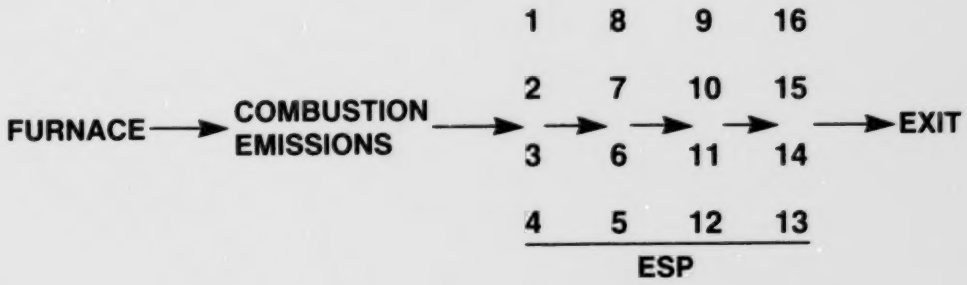

FIGURE 2-2(b) ARRANGEMENT OF ELECTROSTATIC PRECIPITATOR, ESP2, SAMPLING POINTS AT BATTLE RIVER GENERATING STATION

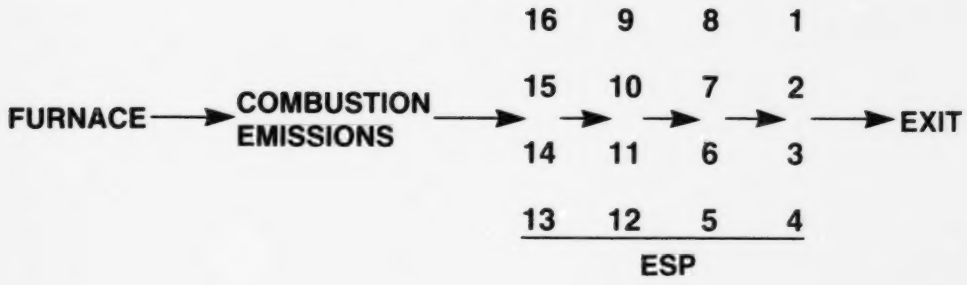

FIGURE 2-3(a) ARRANGEMENT OF ELECTROSTATIC PRECIPITATOR, ESP1, SAMPLING POINTS AT LINGAN GENERATING STATION

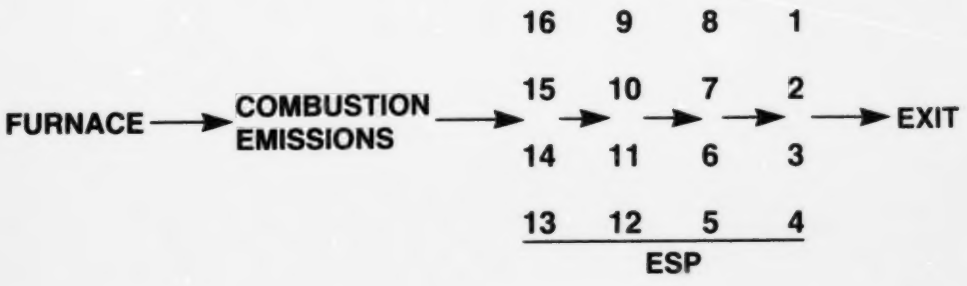

FIGURE 2-3(b) ARRANGEMENT OF ELECTROSTATIC PRECIPITATOR, ESP2, SAMPLING POINTS AT LINGAN GENERATING STATION

3 ANALYTICAL PROTOCOLS

3.1 Polyaromatic Hydrocarbon Extraction Comparison

3.1.1 Toluene Extraction. A 20-g portion of ash was accurately weighed into an Erlenmeyer flask and 200 mL of 1N HCl added. The mixture was shaken on a wrist-action shaker for 2 hours. The sample was allowed to settle and the supernatant filtered through a glass fibre filter. The ash was rinsed with organic-free water and filtered. The ash and filter paper were removed and air-dried in a fume hood. The HCl solution and water rinse were extracted twice in a separatory funnel with 60 mL of methylene chloride, dried with Na_2SO_4, and evaporated on a rotary evaporator to 2 to 3 mL.

The air-dried ash was mixed with precleaned sodium sulphate (30 g) and transferred to a clean glass thimble containing a clean plug of glass wool. The ash was covered with another plug of glass wool and the thimble placed into a soxhlet extractor where its content was extracted with 250 mL of toluene for 24 hours. The toluene extract was removed from the extractor and the methylene chloride extract added to it. The combined extracts were evaporated on a rotary evaporator to 2 to 3 mL and transferred with isooctane rinses to a graduated centrifuge tube. The final volume of this extract was adjusted to 1.0 mL, using dry nitrogen gas, for analysis by full-scan electron impact/gas chromatography-mass spectrometry.

3.1.2 Benzene Extraction. A 20-g portion of ash was accurately weighed into a beaker and 10 mL of organic-free water added. The mixture was homogenized and subdivided into samples. A wet sample was then mixed with 30 g of precleaned $Na_2 SO_4$. The mixture was transferred to a clean glass thimble containing a clean plug of glass wool. The ash was covered with another plug of glass wool. The thimble was placed into a soxhlet extractor and its content extracted with 250 mL of benzene for 24 hours. The benzene extract was removed, evaporated on a rotary evaporator to 2 to 3 mL, and transferred with isooctane rinses to a graduated centrifuge tube. The final volume of this extract was adjusted to 1.0 mL, using dry nitrogen gas, for analysis by full-scan electron impact gas/chromatography-mass spectrometry.

3.1.3 Instrument Conditions. The instrumental conditions used for the identification phase of the study are summarized here:

Gas Chromatography

Column: 30M DB-5 by 0.25 mm I.D. 0.2 µm film thickness

Temp. program:	50°C for 2 minutes - 120°C @ 10°C/min, 260°C @ 8°C/min; hold for 20 minutes
Flow:	20 cm^3/min He
Injection mode:	splitless, 1 min inject @ 25 s
Split:	30 mL/min
Septum sweep:	5 mL/min
Interface:	direct couple, transfer line @ 270°C

Mass Spectrometry

Ionization mode:	Electron impact
Electron energy:	70 eV
Electron multiplier:	1070 V @ 1-5 x 10^6 gain
Scan:	90 to 550 u in 0.95 s with bottom hold for 0.5 s
Ion source:	170°C

3.1.4 Quality Control. A complete method blank was prepared and processed through the two protocols described in Sections 3.1.1 and 3.1.2 to ensure that only contaminants originating from the samples were reported as ash contaminants.

While in the soxhlet thimble, each sample analyzed was spiked before extraction with ϕ_{10}-anthracene (12.5 µg total spike) as a surrogate standard to monitor extraction efficiency. In addition, each sample extract was spiked, just before GC/MS analysis, with 300 µg of ϕ_3-2,4-dichlorophenol as an internal standard to monitor and correct for injection variability.

In the GC/MS analysis of the extracts, a mixed standard of base, neutral, and acid priority pollutants at 2 ng and 10 ng per compound was analyzed along with the samples to assist in contaminant identification and quantitation, check the GC/MS sensitivity, and assess peak symmetry.

3.2 Analysis of Polyaromatic Hydrocarbons, Polychlorinated Dibenzofurans, and Polychlorinated Dibenzo-ρ-Dioxins

3.2.1 Extraction. A 25-g ash sample was weighed into a glass-stoppered Erlenmeyer flask and 200 mL of 1N HCl added to the flask. Each sample was shaken on a wrist-action shaker for 2 hours. The sample was allowed to settle and the supernatant filtered through a glass fibre filter. The ash was rinsed with organic-free water and filtered again. The filtrate was removed and air-dried in a fume hood. The HCl and water rinses were extracted with toluene in a separatory funnel and saved for subsequent use in the soxhlet extraction of the ash. The air-dried ash was charged into a glass thimble

containing clean glass wool. The ash was covered with precleaned glass wool, and the thimble placed into the soxhlet extraction apparatus. The toluene extract of the acid and rinses was used to extract the ash once every 15 minutes for 24 hours.

After the extraction apparatus had cooled, the toluene solution was removed and reduced in volume to 2 to 3 mL on a rotary evaporator, and transferred with isooctane rinses to a calibrated centrifuge tube, where it was made up to 5.0 mL. For the analysis of polyaromatic hydrocarbons, 1 mL of the extract was taken for clean-up and the remaining 4 mL was evaporated to 1 mL for clean-up and analysis of PCDD and PCDF.

3.2.2 Clean-up.

Polyaromatic hydrocarbons. A micro-alumina column was prepared by plugging a clean disposable pipette (4 cm long, 5 mm I.D.) with a piece of glass wool that had previously been washed with acetone and dried. The column was filled to 5 cm with alumina and compacted by gentle tapping. A layer of 0.5 cm of anhydrous Na_2SO_4 was placed on the top of the alumina.

The micro-alumina column was washed first with 7 mL of hexane and twice more with additional 7-mL aliquots of hexane. Each aliquot was permitted to drain just above the top of the adsorbent.

The concentrated sample extract was delivered to the micro-alumina column with a disposable pipette followed by two 1-mL hexane rinses of the sample tube.

The column was eluted with hexane until 10 mL had been collected. This fraction was discarded. PAH were eluted from the column with 10 mL of toluene followed by 3 mL of methylene chloride. The fraction was collected in a 15-mL graduated centrifuge tube.

The toluene-methylene chloride eluant was concentrated by evaporation until just dry and made up to 1.0 mL with methylene chloride for GC/MS analysis.

Polychlorinated dibenzofurans and dibenzo-p-dioxins. A multiple chromatographic column technique was used for clean-up of the concentrated extracts.

The first column was a multilayer column carefully filled with the following:

1.0 g of silica (bottom layer),
2.0 g of 33% 1 M sodium hydroxide on silica,
1.0 g of silica,
4.0 g of 44% concentrated sulfuric acid on silica,
2.0 g of silica, and
enough sodium sulfate for a 1-cm layer.

The column was prewashed with 30 mL of hexane which was then discarded. The sample extract was transferred to the column followed by three 5-mL hexane rinses of the centrifuge tube. An additional 30 mL of hexane was then passed through the column. The total eluate was collected in a 250-mL flask. Isooctane was added to the eluate which was then concentrated to about 1 mL. The concentrated eluate from the first column was then ready for chromatography on a series of two columns: Column A and Column B.

Column A contained 1.5 g of 10% silver nitrate on silica in a disposable pipette. The column was prewashed with 10 mL of hexane. When the column prewash had drained, the concentrated isooctane eluate was introduced into the column followed by three 5-mL hexane rinses of the flask. The column was washed with an additional 10 mL of hexane. When the hexane had drained, the column was discarded. The extract was concentrated to 2 mL of isooctane on a rotary evaporator. This concentrated isooctane extract was then ready for delivery to a 5-cm (1.5-cm I.D.) alumina column (Column B) which had been prewashed with 15 mL of 2% methylene chloride in hexane. The reservoir was rinsed four times with 2 mL of 2% methylene chloride in hexane, and the rinse passed through the alumina column. An additional 20 mL of the 2% eluate was passed through the column. The receiving flask was changed, and the PCDD and PCDF were eluted from the column using 30 mL of 50% methylene chloride in hexane. This fraction was concentrated on a rotary evaporator to about 1 mL and transferred with hexane rinses to a Reactivial. The extract was then blown down with dry nitrogen gas until just dry and taken up in 25 µL of isooctane for GC/MS analysis.

3.2.3 Instrumental Conditions for PCDD/PCDF Analysis.

Gas Chromatography

Injection port:	270°C
Split:	closed
Septum sweep:	4 mL/min
Column flow:	He @ 20 cm/s
Column:	30M by .25 mm DB5
Oven temp. profile:	80°C for 2 min, to 220° @ 12°C/min 220°C to 270°C @ 8°C/min; hold for 20 minutes
GC/MS interface:	direct couple
Transfer area:	270°C

Mass Spectrometry for T_4CDD/T_4CDF Analysis

Ionization mode:	electron impact
Electron energy:	70 eV
Filament emission:	0.5 A
Electron multiplier:	1400 V @ 5 x 10^6 gain
Ionizer temperature:	170°C
Scan (positive ions):	7-ion multiple-ion detection
Ion residence time:	0.11 s/ion
Total scan time:	1.0 s
Ions TCDF:	304, 306, 312*
Ions TCDD:	320, 322, 332*, 334*
	(* denotes labelled standard ions)

Mass Spectrometry for P_5 - O_8 CDD/CDF Analysis

Ionization mode:	chemical ionization
Reagent gas:	CH_4 @ 0.48 TORR (makeup only)
Electron energy:	70 eV
Filament emission:	0.5 A
Electron multiplier:	1400 V @ 5 x 10^6 gain
Ionizer temperature:	60°C
Scan (negative ions):	limited scan range (330 to 480 u)
Total scan time:	1.0 s

3.2.4 Instrumental Conditions for PAH Analysis.

Gas Chromatography

Column:	30M DB-5 x 0.25 mm I.D., 0.2-mm film thickness
Temp. program:	50°C for 2 min - 120°C @ 10°C/min - 260°C @ 8°C/min; hold 20 minutes
Flow:	20 cm^3/min He
Injection mode:	splitless, 1 min inject @ 25 s
Split:	30 mL/min
Septum sweep:	5 mL/min
Interface:	direct couple, transfer line @ 270°C

Mass Spectometry

Ionization mode:	electron impact

Electron energy:	70 eV
Electron multiplier:	1070 V 1 to 5 x 10^6 gain
Scan:	90 to 550 u in 0.95 s with bottom hold .05 s
Ion source:	ionizer @ 170°C

3.2.5 Quality Control. In the analysis of the ash samples, standards of ϕ_{10}-anthracene, 2,3,7,8-TCDD ($^{13}C_{12}$), and OCDD ($^{13}C_{12}$) were used as surrogate standards. These were spiked onto the HCl-treated ash samples before soxhlet extraction. The ϕ_{10}-anthracene was spiked to a total level of 24 µg, which corresponds to about 1 ppm for a 25-g sample. The dioxins were spiked at a level of 0.4 ppb for a 25-g sample.

The sample data are not corrected for the recoveries of the labelled standards, but recoveries for these spikes are reported along with the analytical data for each sample.

Method blanks were processed through the entire analytical procedure to assess and correct for any method-incurred contamination.

A standard reference material of urban dust (National Bureau of Standards: SRM-1649), which had been certified for some PAH, was analyzed along with the samples to provide an assessment of the accuracy of the PAH analyses.

According to Dr. Clarence Haile at the Midwest Research Institute, an ash reference material for dioxins and furans had not yet been developed and, due to lack of funding, was not expected in the near future.

3.2.6 Total Extractable Organic Halogens. Portions of the PAH extracts produced as described in Section 3.2.1 were used for direct analysis of total extractable organic halogen (TEOX). Analysis of each extract was performed by its injection (1 to 5 µL) into a Dohrmann MCTS-20 microcoulometer. The temperature at the inlet of the furnace was 600°C, at the centre 800°C, and at the outlet 850°C. The halogenated organics were pyrolyzed to HX and detected by titration with subsequent signal integration. Data were calculated as ng Cl/g based on calibrations with known concentrations of organochlorine compounds.

The microcoulometer was standardized at least twice a day through injection of organochlorine standards. Solvent blanks and method blanks were run to correct for any method-incurred contamination. Duplicate analysis of some sample extracts was performed to assess the repeatability of sample injections. Extracts from the standard reference material of urban dust were also analyzed for TEOX to provide a preliminary database for comparison in any future studies on combustion ashes.

4 RESULTS AND DISCUSSION

Samples of bed ash and fly ash from the AFBC unit were each extracted in duplicate using the benzene-soxhlet technique and the toluene-soxhlet technique. After review of the AFBC ash data, the fly ash sample from the Poplar River generating station was also analyzed by the toluene soxhlet extraction technique. This section of the report contains these results. GC/MS chromatograms and spectra are presented in Appendix A.

4.1 Comparison of Methods

Full-scan GC/MS analysis of the bed and fly ash samples revealed significant differences in PAH concentration. Whereas no PAH were detected in the bed ash (detection limits of 0.01 to 0.04 µg/g), high ppb concentrations were found in the fly ash. The fly ash sample provided a good basis for comparing the two extraction techniques.

The results from toluene and benzene extractions (see Table 4-1) show that the PAH in order of decreasing concentration were

phenanthrene,
fluoranthene,
naphthalene,
chloronaphthalene,
benz(a)anthracene, and
pyrene.

With the exception of pyrene, every PAH found was higher in the samples prepared by toluene extraction. The pyrene concentration determined by benzene extraction was 0.02 µg/g, whereas none was detected (<0.01 µg/g) in the toluene extracts.

The data presented in Table 4-1 are corrected for response of the internal standard ϕ_3-2,4-dichlorophenol added just before sample injection, but the data are not corrected for the recovery of the surrogate standard ϕ_{10}-anthracene. The recovery of the surrogate standard was higher for the benzene extraction than for the toluene extraction, but the concentrations of all but one of the PAH in the ash were higher for the toluene-extracted samples.

The lack of detected PAH in the bed ash samples limits the comparison of extraction techniques to the fly ash samples only, and therefore the comparison must be considered qualitative only. These results indicate that for PAH in fly ash the toluene soxhlet extraction technique provides higher extraction efficiency than the benzene

TABLE 4-1 COMPARISON OF EXTRACTION TECHNIQUES FOR PAH IN SUMMERSIDE BAGHOUSE ASH

	Toluene Extraction (μg/g)			Benzene Extraction (μg/g)		
	No. 1	No. 2	Mean	No. 1	No. 2	Mean
Naphthalene	0.05	0.38	0.22	0.25	0.08	0.17
Cl-naphthalene	0.14	0.14	0.14	0.09	0.05	0.07
Phenanthrene	1.29	0.54	0.92	0.69	0.53	0.61
Anthracene	0.02	<0.01	<0.01	0.01	<0.01	<0.01
Fluoranthene	0.33	0.15	0.24	0.20	0.12	0.16
Pyrene	<0.01	<0.01	<0.01	0.02	0.01	0.02
Chrysene	0.03	<0.02	<0.02	<0.02	<0.02	<0.02
Benz(a)anthracene	0.13	0.07	0.10	<0.02	0.06	0.04
d_{10}-anthracene (%)	77.6	49.0	63.3	99.0	80.3	90.0

soxhlet extraction technique. However, another aspect of the two extraction techniques, which must also be considered, is the production of artifacts in the extraction process, which can complicate the extract analysis with regard to characterization, if non-GC/MS techniques are used.

4.2 Characterization

The AFBC bed ash contained the lowest number and concentration of trace organics of the ashes analyzed. The benzene extracts of the bed ash showed the presence of the internal and surrogate standards, two phthalate blank peaks, and two sulphur peaks. The sulphur peaks correspond to S_6 (molecular weight: 192) and S_8 (molecular weight: 256). Both spectra produced excellent matches (>900 out of 1000) with library spectra.

The toluene extracts of the AFBC bed ash produced a greater number of compounds at much higher concentrations than the benzene extractions. In addition to those compounds found with benzene extraction, the extracts contained a series of benzyl compounds and another sulphur compound, S_7 (molecular weight: 224). The benzyl compounds were the same as those previously reported by Zenon (1983). Benzyl alcohol, C-14 benzyl compounds, bis(phenylmethyl) sulphide, bis(phenylmethyl) disulphide, and a C-21 benzyl compound were all detected in the toluene extracts. (Spectra are presented in Appendix A.) Subsequent review of selected ion plots of the benzene extracts of bed

ash showed no detectable amounts of these benzyl compounds. In addition, selected ion plotting showed no detectable levels of PAH in either the benzene or toluene extracts.

Analysis of the fly ash samples, however, revealed a number of polyaromatic hydrocarbons and polyaromatic heterocycles in both the benzene and the toluene extracts. Compounds found in these extracts included naphthalene, quinoline, acenaphthene, chloronaphthene, 9H-fluorenone, phenanthrene, fluoranthene, dibenzofuran, and dibenzothiophene. In all cases, the toluene extracts showed higher levels of these contaminants than the benzene extracts. Also, a trichlorophenol isomer was found in the toluene extracts, which was not found in the benzene extracts.

The same results concerning benzyl compounds were found in the fly ash samples and in the bed ash samples: no benzyl compounds were detected in the benzene extracts, whereas the toluene extracts contained varying amounts of these contaminants.

Sulphur compounds S_6 and S_8 were found in both the benzene and the toluene extracts of the fly ash samples.

The Poplar River PCF fly ash was analyzed only with the toluene soxhlet extraction technique. The results for this ash showed no detectable levels of polyaromatic hydrocarbons or polyaromatic heterocycles. The contaminants detected in this sample were again the same benzyl compounds found in every toluene extract. No sulphur (S_6 or S_8) was detected in this sample, unlike the fly ash sample from Poplar River analyzed previously (Zenon, 1983).

According to these results then, only the toluene extracts contain the broad array of benzyl compounds at very high concentration. Yet, if they were ash contaminants, it would be reasonable to expect that benzene extraction also would provide some extraction of these compounds, given the structural similarity of many of the benzyl compounds with polyaromatic hydrocarbons. Since they were not found in the benzene extracts, they must be artifacts produced during the toluene extraction.

In future this finding should be considered prior to the analysis of combustion ashes for purposes of characterization or for such specific trace organics as PAH. These benzyl compounds do not interfere in the analysis of PAH by GC/MS but may interfere if the analysis is either by HPLC or by gas chromatography. In full-scan GC/MS characterizations, high concentrations of these artifacts can also mask components occurring at low concentrations.

4.3 Polyaromatic Hydrocarbons

Twenty-three ash samples and two portions of the standard reference material were analyzed for 15 polyaromatic hydrocarbons. Two complete method blanks were also analyzed. The reverse search identification and quantitation procedure as well as ion plots for all PAH ions were used for quantitation.

The data for all samples are presented in Table 4-2 along with the recovery data for the surrogate standard, ϕ_{10}-anthracene.

PAH concentrations in these fly ash samples were generally low. Phenanthrene, naphthalene, fluoranthene, and pyrene were the only PAH detected.

Method blanks contained none of the 15 PAH at the detection limits of the analysis.

Recovery of the surrogate standard, ϕ_{10}-anthracene, averaged 49 $\pm$ 26 percent for all samples; a lower percentage was recovered from the Lingan samples than from the Battle River or Poplar River samples. These recoveries compare favourably with recoveries of 44 $\pm$ 18 percent and 26 $\pm$ 18 percent for ϕ_8-naphthalene reported by Haile (1983) in two different samples of ESP ashes.

The analysis of the standard reference material of urban dust also compared well with the certified values for all PAH, except indeno (1,2,3-$\psi\phi$) pyrene. The data for these analyses are presented in Table 4-3 along with the NBS reference values.

4.4 Polychlorinated Dioxins and Dibenzofurans

Electron-impact multiple-ion detection (EI/MID) GC/MS analysis was performed for tetrachlorodioxins and -furans, and negative-ion chemical ionization (NCI) GC/MS analysis was performed for the pentachloro- to octachlorodioxins and -furans.

Besides the PCF fly ash samples, two samples of the reference material of urban dust along with two method blanks were analyzed. Every sample was spiked with surrogate standards of carbon-13 labelled T_4CDD and O_8CDD.

The analytical data for all samples are summarized in Table 4-4 along with the recoveries of the two surrogate standards.

The data reveal no detectable levels of tetrachlorodioxins in any of the samples analyzed and only a few detections, at very low concentrations, of any other dioxin congeners.

Polychlorinated dibenzofurans, however, particularly pentachlorodibenzofurans, were detected at higher concentrations in many of the PCF ash samples. Hexachlo-

TABLE 4-2 POLYAROMATIC HYDROCARBONS IN PCF FLY ASHES (µg/g)

Source: Lingan

Compound	Detect. Limits	ESP 1-2	ESP 1-4	ESP 1-7	ESP 1-11	ESP 1-15	ESP 2-2	ESP 2-4	ESP 2-11
Naphthalene	0.02	0.05	ND	0.06	<0.02	ND	0.13	0.16	<0.02
Acenaphthylene	0.02	ND	ND	ND	ND	ND	ND	ND	ND
Acenaphthene	0.02	ND	ND	ND	ND	ND	ND	ND	ND
Cl-naphthalene	0.02	ND	ND	ND	ND	ND	ND	ND	ND
Fluorene	0.02	ND	ND	ND	ND	ND	ND	ND	ND
Phenanthrene	0.02	NA	NA	0.02	0.68	ND	ND	ND	0.04
Anthracene	0.02	ND	ND	ND	ND	ND	ND	ND	ND
Fluoranthene	0.02	ND	ND	0.03	ND	ND	0.05	0.02	ND
Pyrene	0.02	ND	ND	0.03	ND	ND	0.05	0.02	ND
Chrysene	0.02	ND	ND	ND	ND	ND	ND	ND	ND
Benzo(a)anthracene	0.02	ND	ND	ND	ND	ND	ND	ND	ND
Benzo(e)pyrene	0.05	ND	ND	ND	ND	ND	ND	ND	ND
Indeno(1,2,3-c,d)pyrene	0.10	ND	ND	ND	ND	ND	ND	ND	ND
Dibenzo(a,h)anthracene	0.10	ND	ND	ND	ND	ND	ND	ND	ND
Recovery d_{10}-anthracene (%)		17.9	24.5	47.8	38.3	84.5	5.1	18.4	16.5

Source: Poplar River

Compound	Detect. Limits	ESP 3-B5
Naphthalene	0.02	<0.02
Acenaphthylene	0.02	ND
Acenaphthene	0.02	ND
Cl-naphthalene	0.02	ND
Fluorene	0.02	ND
Phenanthrene	0.02	0.19
Anthracene	0.02	ND
Fluoranthene	0.02	0.03
Pyrene	0.02	0.03
Chrysene	0.02	ND
Benzo(a)anthracene	0.02	ND
Benzo(a)pyrene	0.05	ND
Indeno(1,2,3-c,d)pyrene	0.10	ND
Dibenzo(a,h)anthracene	0.10	ND
Benzo(g,h,i)perylene	0.10	ND
Recovery d_{10}-anthracene (%)		65.3

Source: Battle River

Compound	Detect. Limits	PFA 3-2	PFA 3-4	PFA 3-6	PFA 3-8	PFA 3-10	PFA 3-12	PFA 3-14	PFA 3-16	PFA 4-2	PFA 4-4	PFA 4-6	PFA 4-8	PFA 4-10	PFA 4-16
Naphthalene	0.02	ND	0.02	<0.02	ND	0.03	<0.02	ND	0.49	<0.02	ND	ND	0.02	ND	ND
Acenaphthylene	0.02	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Acenaphthene	0.02	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Cl-naphthalene	0.02	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Fluorene	0.02	ND	ND	ND	ND	ND	ND	ND	<0.02	ND	ND	ND	ND	ND	ND
Phenanthrene	0.02	ND	ND	ND	ND	0.14	ND	ND	<0.02	ND	ND	ND	ND	ND	ND
Anthracene	0.02	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Fluoranthene	0.02	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Pyrene	0.02	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chrysene	0.02	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo(a)anthracene	0.02	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo(a)pyrene	0.05	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Indeno(1,2,3-c,d)pyrene	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	<0.10	ND	ND
Dibenzo(a,h)anthracene	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	<0.10	ND	ND
Benzo(g,h,i)perylene	0.10	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	<0.10	ND	ND
Recovery d_{10}-anthracene (%)		46.4	28.1	76.2	64.8	22.4	88.7	12.0	66.8	80.2	80.4	55.5	78.3	36.1	69.0

TABLE 4-3 PAH STANDARD REFERENCE MATERIAL ANALYSIS

Compound	Amount Recovered (µg/g)	
	NBS Reference Value	Mean Analytical Result
Fluoranthene	7.1 + 0.5	8.0 + 1.4
Pyrene	7.0 + 0.4	7.5 + 0.5
Benzo(a)anthracene	2.6 + 0.3	3.1 + 0.4
Benzo(a)pyrene	2.9 + 0.5	3.7 + 1.5
Benzo(g,h,i)perylene	4.5 + 1.1	4.5 + 1.4
Indeno(1,2,3-c,d)pyrene	3.3 + 0.5	8.5 + 3.0

rodibenzofurans were also detected in many of the samples, but at lower concentrations than those of the pentachlorodibenzofurans.

The recoveries of T_4CDD ($^{12}C_{13}$) for all samples averaged 64 + 34 percent, whereas the recoveries of O_8CDD averaged 81 + 39 percent. No comparison can be made with the MRI study on combustion emissions (Haile, 1983), because no surrogate spikes were used in that analysis. These values are quite comparable to other recovery data on soils and incinerator ashes.

The data for polychlorinated dibenzo-p-dioxins and furans in the reference urban dust samples is shown in Table 4-5. The data show very high levels of PCDD and significantly lower levels of PCDF. The duplicate analysis of this material showed good agreement within the sample: relative standard deviations of less than $\pm$10 percent for all dioxin and furan congeners.

4.5 Total Extractable Organic Halogen

Twenty-three fly ash samples from three PCF power generating stations were extracted and analyzed for total extractable organic halogen (TEOX). All data were corrected for an average method blank of 3.8 ng Cl/µL

The data obtained for the PCF fly ashes are presented in Table 4-6 along with the TEOX data obtained on two quality assurance standard reference materials (NBS SRM 1649 - Urban Dust).

TABLE 4-4 POLYCHLORINATED DIBENZO-ρ-DIOXINS AND FURANS IN PULVERIZED COAL-FIRED POWER STATION FLY ASHES (ng/g)

Source: Battle River

	PFA 3-2	PFA 3-4	PFA 3-6	PFA 3-8	PFA 3-10	PFA 3-12	PFA 3-14	PFA 3-16
Dibenzo-ρ-Dioxins								
TCDD	ND(0.02)	ND(0.03)	ND(0.03)	ND(0.02)	ND(0.02)	ND(0.01)	ND(0.03)	ND(0.03)
P_5CDD	0.006	ND(0.002)	ND(0.001)	ND(0.002)	ND(0.001)	ND(0.001)	ND(0.001)	ND(0.001)
H_6CDD	ND(0.001)	ND(0.001)	ND(0.001)	ND(0.001)	ND(0.001)	ND(0.001)	ND(0.002)	ND(0.001)
H_7CDD	ND(0.001)	ND(0.001)	ND(0.001)	ND(0.001)	ND(0.002)	ND(0.002)	ND(0.002)	ND(0.002)
OCDD	ND(0.003)	ND(0.002)	ND(0.002)	ND(0.002)	ND(0.002)	0.002	ND(0.002)	ND(0.002)
Dibenzofurans								
TCDF	0.02	ND(0.02)	0.07	ND(0.02)	ND(0.03)	0.09	ND(0.01)	0.08
P_5CDF	0.026	0.014	0.013	0.0.12	0.014	0.025	0.01	0.024
H_6CDF	ND(0.002)	0.002	0.005	0.007	0.004	0.008	ND(0.002)	0.01
H_7CDF	ND(0.002)	ND(0.002)	ND(0.002)	0.004	ND(0.001)	ND(0.001)	ND(0.001)	ND(0.001)
OCDF	ND(0.001)	ND(0.001)	ND(0.001)	ND(0.001)	ND(0.001)	ND(0.001)	ND(0.001)	ND(0.001)
Recovery T_4CDD*	61	36	108	107	57	67	44	53
Recovery OCDD*	37	147	103	121	50	51	39	48

	PFA 4-2	PFA 4-4	PFA 4-6	PFA 4-8	PFA 4-10	PFA 4-16
Dibenzo-ρ-Dioxins						
TCDD	ND(0.02)	ND(0.01)	ND(0.01)	ND(0.02)	ND(0.02)	ND(0.01)
P_5CDD	ND(0.001)	0.014	ND(0.002)	ND(0.001)	0.01	ND(0.002)
H_6CDD	ND(0.001)	ND(0.001)	ND(0.001)	ND(0.001)	ND(0.001)	ND(0.001)
H_7CDD	ND(0.001)	ND(0.001)	ND(0.001)	ND(0.001)	ND(0.002)	ND(0.001)
OCDD	0.007	ND(0.002)	ND(0.002)	ND(0.002)	ND(0.002)	ND(0.002)
Dibenzofurans						
TCDF	0.04	ND(0.01)	ND(0.01)	ND(0.01)	ND(0.03)	0.03
P_5CDF	0.062	0.022	0.017	0.013	0.0003	0.092
H_6CDF	0.042	0.016	0.006	0.01	ND(0.002)	0.054
H_7CDF	0.028	ND(0.001)	ND(0.002)	ND(0.001)	ND(0.002)	0.021
OCDF	ND(0.001)	ND(0.001)	ND(0.001)	ND(0.001)	ND(0.001)	0.001
Recovery T_4CDD*	113	84	20	27	133	46
Recovery OCDD*	106	89	47	30	122	140

Source: Poplar River	ESP 3-B5
Dibenzo-ρ-Dioxins	
TCDD	ND(0.02)
P_5CDD	ND(0.002)
H_6CDD	ND(0.001)
H_7CDD	0.002
OCDD	0.012
Dibenzofurans	
TCDF	ND(0.01)
P_5CDF	0.03
H_6CDF	0.003
H_7CDF	0.006
OCDF	ND(0.001)
Recovery T_4CDD*	78
Recovery OCDD*	103

Source: Lingan

	ESP 1-2	ESP 1-4	ESP 1-7	ESP 1-11	ESP 1-15	ESP 2-2	ESP 2-4	ESP 2-11
Dibenzo-ρ-Dioxins								
TCDD	ND(0.01)	ND(0.02)	ND(0.01)	ND(0.03)	ND(0.03)	ND(0.01)	ND(0.03)	ND(0.01)
P_5CDD	ND(0.001)	ND(0.002)	ND(0.002)	ND(0.002)	ND(0.001)	ND(0.001)	ND(0.002)	ND(0.001)
H_6CDD	ND(0.001)	ND(0.002)	ND(0.002	0.001	ND(0.003)	ND(0.001)	ND(0.001)	ND(0.001)
H_7CDD	ND(0.001)	ND(0.003)	ND(0.002)	ND(0.002)	ND(0.001)	ND(0.001)	ND(0.002)	ND(0.002)
OCDD	ND(0.002)	ND(0.002)	ND(0.002)	0.008	0.006	ND(0.002)	0.010	ND(0.002)
Dibenzofurans								
TCDF	ND(0.01)	ND(0.02)	ND(0.01)	ND(0.03)	ND(0.02)	ND(0.01)	ND(0.02)	ND(0.01)
P_5CDF	0.011	0.023	0.008	0.008	0.007	0.005	0.011	0.021
H_6CDF	0.003	0.001	0.005	0.003	ND(0.001)	ND(0.002)	ND(0.002)	0.003
H_7CDF	ND(0.001)	ND(0.001)	ND(0.001)	0.003	0.002	ND(0.001)	0.038	ND(0.002)
OCDF	ND(0.001)	ND(0.001)	ND(0.001)	ND(0.001)	ND(0.002)	ND(0.002)	0.010	ND(0.001)
Recovery T_4CDD*	26	36	39	108	118	31	58	45
Recovery OCDD*	41	46	62	116	122	25	83	122

TABLE 4-5 PCDD/PCDF IN STANDARD REFERENCE MATERIAL OF URBAN DUST (ng/g)

Compound	Sample No. 1	Sample No. 2	Mean
Dioxins			
T_4CDD	ND(0.05)	ND(0.05)	ND(0.05)
P_5CDD	0.720	1.37	1.05 + .45
H_6CDD	2.01	12.16	2.14 + .13
H_7CDD	14.63	12.16	13.40 + 1.2
O_8CDD	93.32	81.12	87.2 + 6.1
Furans			
T_4CDF	ND(0.05)	ND(0.05)	ND(0.05)
P_5CDF	0.760	1.80	1.28 + 0.74
H_6CDF	0.484	2.06	1.27 + 1.10
H_7CDF	4.64	3.81	4.22 + 0.42
O_8CDF	1.38	1.31	1.34 + 0.37
Recovery T_4CDD (%)	44	62	53 + 9

The data show a range of TEOX concentrations in these fly ash samples from <0.02 to 14.81 µg Cl/g. One sample from Battle River BR-PFA 3-10 contained a concentration of 2.34 µg Cl/g, well above all other samples, and has been excluded as an outlier.

The only sample collected at Poplar River (PR ESP3-B5) contained 5.25 µg Cl/g. Samples collected from Battle River ranged from <0.02 to 5.42 µg Cl/g (excluding the very high sample) with a mean TEOX concentration of 0.09 µg Cl/g.

The range of TEOX concentrations found in fly ash samples collected at Lingan was 0.55 to 14.81 µg Cl/g with a mean concentration of 4.28 µg Cl/g.

Size segregation of the fly ash on the different electrostatic precipitators (ESP) collectors commonly occurs (L. Dwyer, Environment Canada, personal communication) with the finest particles being more abundant on ESP collectors at the outlet side of the ESP bank. The locations in the ESP where samples were collected were shown previously in Figures 2-1 through 2-3. The correlation of TEOX ash concentration with the ESP row from where the sample was taken was evaluated by using linear regression analysis. Data were pooled from both ESP collectors within each of the sites at Battle River and Lingan, and linear regression analysis performed separately on the data from these sites.

TABLE 4-6 TOTAL EXTRACTABLE ORGANIC HALOGEN IN PCF COMBUSTION FLY ASH SAMPLES

Sample Identification	Blank Corrected TEOX µg Cl/mL	Sample WT. (g) For TEOX Analysis	TEOX µg Cl/g
PRESP 3-B5	21.3	4.06	5.25
BR-PFA 3-2	0	4.04	< 0.02
BR-PFA 3-4	2.9	4.26	0.68
BR-PFA 3-6	2.8	4.06	0.69
BR-PFA 3-8	0	4.08	< 0.02
BR-PFA 3-10	956	4.08	234.3
BR-PFA 3-12	0.8	4.04	0.19
BR-PFA 3-14	22.1	4.08	5.42
BR-PFA 3-16	11.2	4.06	2.76
BR-PFA 4-2	0.1	4.22	0.02
BR-PFA 4-4	0	4.1	< 0.02
BR-PFA 4-6	0.3	4.98	0.06
BR-PFA 4-8	0	4.08	< 0.02
BR-PFA 4-10	4.6	4.18	1.1
BR-PFA 4-16	3.1	4.1	0.76
LNS-ESP 1-2	15.7	4.14	3.79
LNS-ESP 1-4	6.7	4.06	1.65
LNS-ESP 1-7	12	4.27	2.81
LNS-ESP 1-11	20.3	4.22	4.81
LNS-ESP 1-15	2.8	4.56	0.61
LNS-ESP 2-2	27.2	3.06	8.89
LNS-ESP 2-4	54.5	3.68	14.81
LNS-ESP 2-11	2.3	4.22	0.55
Urban Dust No. 1	523	0.4	1308
Urban Dust No. 2	612	0.42	1457

In Figure 4-1, the data on the eight ash samples from Lingan are plotted and a least-squares line drawn. The coefficient of correlation for this data is 0.560, which is significant at a confidence interval between 85 and 90 percent.

The data for the 13 ash samples from Battle River are shown in Figure 4-2 along with the resulting least-squares plot. The coefficient of correlation obtained on this data is 0.672, which is significant at the 99-percent level of confidence.

The correlation of TEOX with total PCDD/PCDF was also evaluated using linear regression analysis: a coefficient of correlation of 0.064 was determined. On the

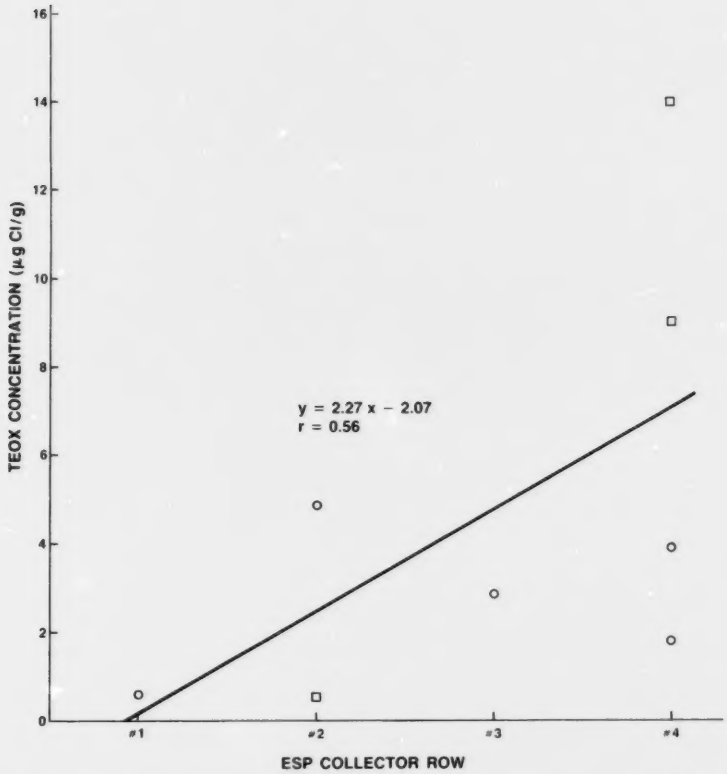

FIGURE 4-1 TEOX CONCENTRATION vs. ESP COLLECTOR AT LINGAN

basis of these data, no significant correlation exists between TEOX concentration and PCDD/PCDF concentration in the PCF fly ashes tested.

The TEOX concentrations of <0.02 to 14.81 µg Cl/g in PCF fly ash samples are considerably lower than the TEOX concentrations of 1382 ± 105 µg Cl/g found in the urban dust samples. The duplicate analysis of the urban dust samples produced a relative standard deviation of ± 7.6 percent.

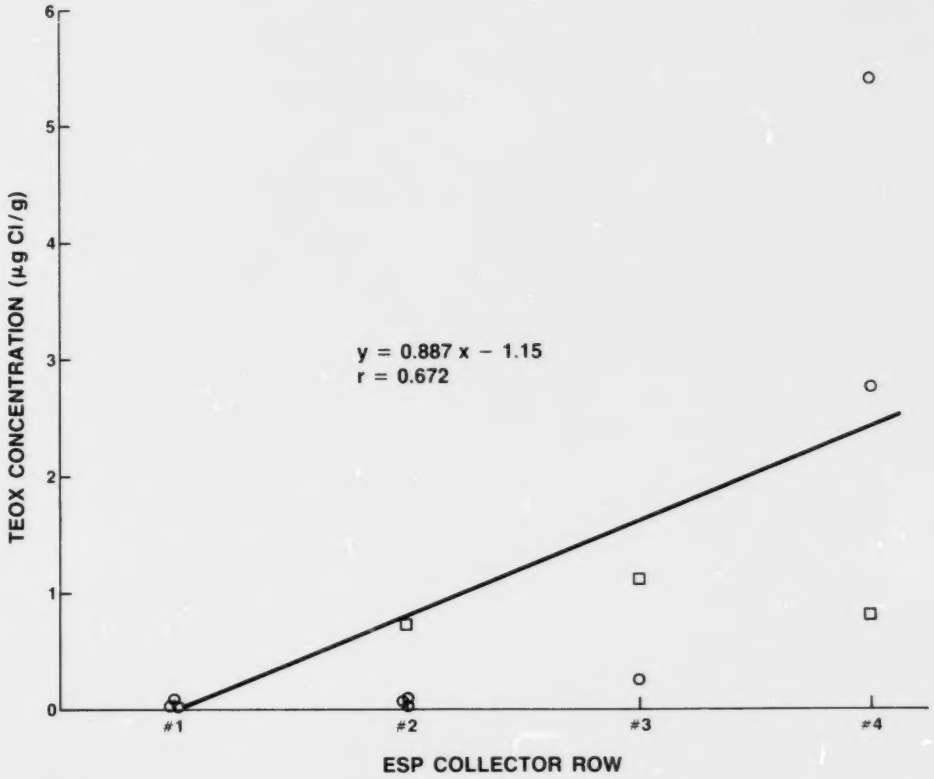

FIGURE 4-2 TEOX CONCENTRATION vs. ESP COLLECTOR AT BATTLE RIVER

5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Methods Comparison and Characterization

A comparison of benzene and toluene extractions for the preparation of ash samples reveals that generally, higher extraction efficiencies for polyaromatic hydrocarbons are obtained with toluene extraction. This comparison is limited to a single fly ash sample, since the bed ash sample analyzed was found to contain no detectable PAH.

During the full-scan analyses of ash extracts prepared by both extraction techniques it became evident that benzyl compounds, such as benzyl alcohol, bis(phenylmethyl) sulphide, and C_{14} and C_{21} benzyl compounds, are found only in the toluene extracts. This fact and the expectation of similar solubilities of these compounds in both benzene and toluene and their absence in all method blanks strongly suggest that these benzyl compounds are produced during the toluene soxhlet extraction of acid-washed ash samples.

Preliminary analysis indicates not only that toluene extraction provides higher extraction efficiency than benzene extraction, but that it also results in the formation of numerous benzyl compounds. Future characterizations should not use toluene extraction because of the formation of the compounds which, in turn, can effect subsequent analyses.

5.2 Polyaromatic Hydrocarbons

The analysis of 23 fly ash samples from PCF power generating stations reveals very low concentrations of PAH in these ashes. Phenanthrene, naphthalene, fluoranthene, and pyrene were the only PAH detected in these samples, and always at parts-per-billion concentrations. Alternative analytical techniques, such as high-pressure liquid chromatography with UV and fluorescence detectors or multiple-ion detection GC/MS, would improve the sensitivity for PAH, if this is necessary for mass balance calculations.

5.3 Polychlorinated Dibenzo-p-Dioxins and - Furans

Analysis of 23 PCF ashes for tetrachloro- to octachlorodioxins and furans reveals that PCDD are generally not detectable in these ash samples at concentrations of 1 to 20 parts per trillion. But PCDF, particularly the pentachloro- and hexachlorofurans, were frequently detected in the range of 2 to 40 parts per trillion in these ashes. These findings are consistent with those reported by Zenon (1983) about similar combustion ashes.

The analysis of the NBS reference material of urban dust has shown the presence of significant levels of chlorinated dioxins and chlorinated furans. This material, which has been tested by the NBS, has been shown to be homogeneous with respect to PAH and therefore provides a useful reference material for future comparison studies of methods and for analytical quality control.

5.4 Total Extractable Organic Halogen

TEOX analysis of the extracts from 23 PCF ashes showed concentrations ranging from <0.02 to 14.8 µg Cl/g. The mean TEOX concentration of ashes from Lingan was 4.28 µg Cl/g, whereas the mean value from Battle River was 0.90 µg Cl/g. Analysis of the TEOX data reveals significant correlation of ash TEOX concentration with the location of ESP at which the sample was collected.

The highest values of TEOX were obtained for ashes collected from the final ESP banks at both Lingan and Battle River. It is thought that this relates to the correlation of TEOX with ash particle size; however, data supporting such correlation are still required.

No correlation was found between PCDD/PCDF concentration and TEOX concentration, therefore other halogenated organics must be responsible for the TEOX concentrations. The TEOX concentrations found on the reference material of urban dust were 300 to 1300 times higher than the TEOX concentrations found in Battle River and Lingan ashes. Duplicate analysis of the urban dust reveals that precision of the method is $\pm$ 7.6 percent.

Further analysis at low parts-per-billion concentrations is necessary to determine those compounds contributing to the total extractable organic halogen concentrations in these ash samples.

SECTION B

Summary Report on Trace Organic Contaminants in Ashes from Pulverized Coal-fired Power Generating Stations

6 INTRODUCTION

This summary report on trace organic contaminants in combustion ashes from PCF power generating stations presents a review of data reported by Environment Canada (Lao, 1983), Battelle (1983), Midwest Research Institute (Haile, 1983) and Zenon (1983; 1984).

The primary focus of the review is on PCF ashes from Canadian power generating stations; however, data from other combustion ashes have also been included for comparison.

7 CHARACTERIZATION OF TRACE ORGANICS

Full-scan HRGC/MS analysis of trace organics of raw solvent extracts of PCF fly ash and bed ash samples as well as ashes from atmospheric fluidized-bed combustion units have been reported by Zenon (1983, 1984). With this type of analysis, detection limits for individual contaminants are approximately 0.2 to 0.05 parts per million, provided each contaminant is well separated from other contaminants, so that a contaminant of lower concentration is not obscured by contaminants at higher concentrations.

In the first study (Section A), a broad array of benzyl contaminants were identified by using a toluene extraction procedure for sample preparation. This study (Section B) was designed to determine whether these compounds are ash contaminants or artifacts of the preparation technique. Through comparison with benzene extraction, it was found that all these compounds are, indeed, artifacts of the solvent extraction technique and had limited the identifications of any ash contaminants present at lower concentrations.

PCF fly ashes from Lingan, Poplar River, and Dalhousie have been analyzed by full-scan HRGC/MS, so have ash samples from a fluidized-bed combustor in Summerside and from a pilot-scale fluidized-bed combustor burning both Devco-Prince and Minto coals.

AFBC fly ash samples from Summerside and Devco-Prince as well as Minto coal bed and fly ash samples from a pilot-scale unit were also analyzed.

A comparison of results shows that no detectable levels of aliphatic, chloroaromatic, polyaromatic, or polyaromatic heterocyclic organics have been found in the PCF fly ashes. However, in both the Summerside and the Devco AFBC fly ashes, readily detectable levels of PAH, such as phenanthrene, fluoranthene, pyrene, chrysene, benzo(a)anthracene, fluorenone, and naphthalene, were identified.

Bed ash from both the AFBC unit burning Devco-Prince coal and the combustor at Summerside showed no detectable levels of these polyaromatic hydrocarbons or polyaromatic heterocycles: however, the Minto bed ash (which results from the combustion of Minto coal and approximately 30 percent wood chips) contained low parts-per-million levels of phenanthrene, fluoranthene, pyrene, chrysene, benzo(α)anthracene, indeno(1,2,3-ψ′φ)pyrene, and dibenzo(α′η)anthracene.

The results reported to date indicate that the collected fly ashes from PCF stations contain no detectable contaminants at parts-per-million concentrations, and levels in collected fly ash samples from AFBC units are more highly contaminated with

polyaromatic hydrocarbons and polyaromatic heterocycles. However, it must be noted that the AFBC units from which these samples were obtained are a pilot-scale test facility and a very small demonstration heating unit. As development of fluidized-bed combustion continues, and much larger units of utility size are developed, combustion efficiencies are expected to improve considerably. Correspondingly, the characteristics of the organics in wastes from these units can be expected to change somewhat as well.

8 POLYAROMATIC HYDROCARBONS

A more specific HRGC/MS analysis of ash extracts for PAH after alumina clean-up has been reported by Zenon (1983; 1984) on 34 fly ash samples and 6 bottom ash samples from PCF power generating stations.

The results of these analyses are summarized in Table 8-1. Naphthalene was the most frequently detected PAH in both fly ash and bottom ash samples. Phenanthrene was the least frequently detected PAH; when it was detected, it showed a higher mean concentration. Other PAH, in decreasing order of concentration and detection frequency, are

pyrene,
fluoranthene,
benzo(a)anthracene,
benzo(α)pyrene,
fluorene, and
benzo(λ´η´ι)perylene.

Generally, the same PAH were detected in both fly ashes and bottom ashes. The concentrations of all PAH were sub-ppm in all fly ash samples, whereas two bottom ashes contained low ppm concentrations of phenanthrene and naphthalene.

Battelle (1983) has reported on the PAH emissions from Lingan, Poplar River, and Nanticoke. Their data (Table 8-2) show high mg/h emission rates for many of the PAH not detected in Zenon's analysis of ESP fly ash samples collected at those power generating stations. In addition, several alkylated PAH have also been reported by Battelle that were not found in Zenon's analysis of the ESP ashes.

Findings similar to these have been reported by Haile (1983) in an RDF/coal co-fired power generating station in Ames, Iowa. The data for PAH in the fuels, inlet and outlet flue gases (to and from the ESP), the ESP ash, and bottom ash are shown in Table 8-3. Comparison of the outlet flue gas and the ESP ash concentrations show a similar pattern to that of the Battelle and Zenon data. Low concentrations of PAH were found in the ESP ash and high mg/h emission rates were determined in the outlet flue gas.

All these findings support Natusch's conclusion (1978) that a large proportion of PAH remains in the vapour phase until the flue gas is past the particulate collectors and at or near the stack exit. Apparently emissions of these trace organics from these combustion units are considerably higher than the amounts retained in collected ashes.

TABLE 8-1 SUMMARY OF POLYAROMATIC HYDROCARBONS IN PCF POWER STATION ASHES (Zenon)

Compounds	PCF Fly Ash Samples			
	No. of Samples	No. of Detections	Range of Detected Concentrations (µg/g)	Mean of Detected Values (µg/g)
Naphthalene	34	13	0.02 - 0.49	0.07
Cl-naphthalene	34	0	-	-
Acenaphthylene	34	0	-	-
Acenaphthene	34	0	-	-
Fluorene	34	0	-	-
Phenanthrene	34	5	0.02 - 0.68	0.21
Anthracene	34	0	-	-
Fluoranthene	34	4	0.02 - 0.05	0.03
Pyrene	34	4	0.02 - 0.05	0.03
Chrysene	34	1	0.10	0.10
Benzo(a)anthracene	34	1	0.17	0.17
Benzo(a)pyrene	34	0	-	-
Indeno(1,2,3-c,d)pyrene	34	0	-	-
Dibenzo(a,h)anthracene	34	0	-	-
Benzo(g,h,i)perylene	34	0	-	-

Compounds	PCF Bottom Ash Samples			
	No. of Samples	No. of Detections	Range of Detected Concentrations (µg/g)	Mean of Detected Values (µg/g)
Naphthalene	6	4	0.04 - 2.51	0.89
Cl-naphthalene	6	0	-	-
Acenaphthylene	6	0	-	-
Acenaphthene	6	0	-	-
Fluorene	6	1	0.33	0.33
Phenanthrene	6	2	2.55 - 3.90	3.23
Anthracene	6	1	0.06	0.06
Fluoranthene	6	1	0.27	0.27
Pyrene	6	2	0.24 - 0.47	0.36
Chrysene	6	2	0.21 - 0.26	0.24
Benzo(a)anthracene	6	2	0.41 - 0.74	0.58
Benzo(a)pyrene	6	0	-	-
Indeno(1,2,3-c,d)pyrene	6	0	-	-
Dibenzo(a,h)anthracene	6	0	-	-
Benzo(g,h,i)perylene	6	1	0.29	0.29

TABLE 8-2 SUMMARY OF PAH EMISSIONS (mg/h) (Battelle 1983)

	Power Generating Stations					
	Lingan		Poplar River		Nanticoke	
PAH	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2
Naphthalene	-	-	-	-	-	-
Acenaphthylene	16.3	10.2	-	-	-	-
Acenaphthene	-	17.8	-	-	-	-
Fluorene	-	-	30	36.5	-	-
9,10 Dihydroanthracene	76.7	244	130	182	273	129
Octahydroanthracene	44.8	168	421	48.6	57.4	17.5
1-Methylfluorene	36.7	53.4	200	-	316	122
Phenanthrene	17.2	66.2	190	36.5	43	4.57
Anthracene	-	25.4	110	60.8	143	53.3
1,Methylphenanthrene	14.0	234	190	122	301	152
2,Methylanthracene	67.7	667	90	60.8	273	83.8
9,Methylanthracene	211	1 340	-	-	28.7	-
Fluoranthene	56.3	590	10	134	387	-
Pyrene	**	**	872	1 400	2 650	518
9,10-Dimethylanthracene	149	1 130	721	450	832	533
1,2-Benzofluorene	213	265	-	48.6	602	114
1,1-Binaphthyl	178	407	-	-	-	-
Benzo(a)anthracene	15.5	56	60.1	-	-	-
Benzo(a)phenanthrene	15.5	48.3	20	60.8	-	-
Chrysene	-	10.2	110	-	215	-
9,10-Benzophenanthrene	-	10.2	-	-	-	-
1-Nitropyrene	104	214	562	85.1	201	38.1
Benzo(k)fluoranthene	-	-	140	-	-	-
Benzo(b)fluorathene	23.7	117	190	-	-	-
Benzo(e)pyrene	12.2	22.9	80.2	814	43	38.1
Benzo(a)pyrene	1 550	4 500	140	194	775	45.7
3-Methylcholanthrene	-	-	-	-	-	228
Indeno(1,2,3-c,d)pyrene	-	-	120	-	186	83.8
Dibenzo(a,h)anthracene	-	-	-	72.9	775	206
Benzo(g,h,i)perylene	536	286	802	109	230	122
Total Weight Identified	3 420	11 000	6 270	5 250	9 640	3 470
Total Weight Collected	43 800	88 500	2.64×10^5	1.48×10^5	3.3×10^5	7.68×10^4

** Chemical interference.
- Below limit of detection.

TABLE 8-3 COMPOUNDS QUANTITATED IN THE PRIMARY INPUT AND EMISSION MEDIA FOR THE AMES MUNICIPAL POWER PLANT, UNIT NO. 7 (Haile, 1983)

		Inputs						Emissions							
		Coal		Refuse-derived Fuel		Plant Background Air		Flue Gas Inlet		Flue Gas Inlet		ESP Ash		Bottom Ash	
Compound	Composite Day	Conc. (ng/g)	Input Rate (mg/h)	Conc. (ng/g)	Input Rate (mg/h)	Conc. (ng/dscm)	Input Rate (mg/h)	Conc. (ng/dscm)	Emission Rate (mg/h)	Conc. (ng/dscm)	Emission Rate (mg/h)	Conc. (ng/g)	Emission Rate (mg/h)	Conc. (ng/g)	Emission Rate (mg/h)
Phenanthrene	1	7 550	110 000			0.29	0.04	270	76	390	110	0.3	0.4	32	3.2
	2	9 090	130 000	1 400	3 100	0.6	0.09	420	140	320	100			250	99
	3	15 400	210 000	940	4 100	0.8	0.11	660	200	320	96	0.2	0.2	140	78
	4	8 500	110 000	948	1 800	0.8	0.13	640	200	37	12	0.2	0.2	43	14
	5	18 600	270 000	828	1 800	0.32	0.044	200	54	480	13	0.2	0.2	500	180
Anthracene	1	1 570	23 000					59	16	49	14				
	2	1 840	26 000	296	810	0.17	0.028	57	18	77	26				
	3	1 260	18 000			0.16	0.024	77	22	78	24			24	13
	4	2 120	28 000			0.19	0.030	89	28	46	14				
	5	4 110	59 000					100	28	77	22			130	46
Fluoranthene	1	1 190	17 000			0.36	0.05	70	20	46	13			10	1.0
	2	1 640	23 000	984	1 300	0.7	0.11	240	78	40	13			52	21
	3	3 320	46 000	271	1 200	0.7	0.11	140	42	97	30			30	17
	4	900	12 000	306	580	1.0	0.16	87	28	28	8.8				
	5	3 210	46 000	198	420	0.5	0.07	94	26	130	36			450	160
Pyrene	1	1 340	20 000			0.36	0.05	220	64	110	32			9.0	0.90
	2	1 960	28 000	552	1 500	0.7	0.12	850	280	96	32			64	26
	3	3 810	53 000	436	1 900	0.7	0.11	480	140	250	74			29	16
	4	1 070	14 000	282	530	1.1	0.17	230	74	66	22			6.0	1.9
	5	4 040	58 000	372	790	0.5	0.07	330	90	330	90			420	150
Chrysene	1	370	5 400			0.29	0.04	3.5	1.0			0.3	0.4		
	2	425	6 000	434	1 200	0.40	0.07	28	8.0						
	3	1 060	15 000			0.37	0.06								
	4	238	3 200			0.60	0.09	9.6	3.2						
	5	1 300	19 000			0.38	0.05	2.8	0.76	2.7	0.76			170	58
Benzo(a)pyrene	1					0.07	0.01	21	6.0	13	3.8				
	2					0.17	0.28	64	22						
	3					0.11	0.016	120	38						
	4					0.09	0.015	19	6.2	28	6.0				
	5					0.07	0.008	63	17						
Indeno(1,2,3-c,d)pyrene	1														
	2														
	3														
	4					0.02	0.003								
	5														
Benzo(g,h,i)perylene	1									3.3	0.96				
	2														
	3									22	6.6				
	4					0.09	0.015			4.6	1.5				
	5														

By way of comparison, the two AFBC units for which fly ash samples have been analyzed contained readily detectable levels of several PAH. Both units captured the ash with baghouse rather than ESP devices. The comparison data are presented in Table 8-4.

TABLE 8-4 PAH CONCENTRATIONS IN ATMOSPHERIC FLUIDIZED-BED COMBUSTOR AND PULVERIZED COAL-FIRED FLY ASHES (Zenon)

	Fly Ashes			
	AFBC (Baghouse)			PCF (ESP)
Compounds	Summerside (µg/g)	Devco (µg/g)	Mean Detected Values (µg/g)	Mean Detected Values (µg/g)*
Naphthalene	0.22	-	0.22	0.07
Cl-naphthalene	0.14	-	0.14	-
Acenaphthylene	-	-	-	-
Acenaphthene	-	-	-	-
Fluorene	-	-	-	-
Phenanthrene	0.92	1.15	1.04	0.21
Anthracene	-	-	-	-
Fluoranthene	0.24	1.08	0.66	0.03
Pyrene	-	0.75	0.75	0.03
Chrysene	-	0.72	0.72	0.10
Benzo(a)anthracene	0.10	1.00	0.55	0.17
Benzo(a)pyrene	-	0.16	0.16	-
Indeno(1,2,3-c,d)pyrene	-	-	-	-
Dibenzo(a,h)anthracene	-	-		-
Benzo(g,h,i)perylene	-	-	-	-

* From Table 8-1

In both ashes, the same PAH are present with the exception of chlorcnaphthalene and benzo(a)pyrene, which were present in one of the AFBC fly ashes but not detected in any of the 34 PCF fly ashes. The data is still too sparse on AFBC ashes to permit meaningful comparison of the PAH concentrations.

9 POLYCHLORINATED DIBENZO-ρ-DIOXINS AND FURANS

Previously, ash samples from Canadian PCF power generating stations have also been analyzed by Environment Canada (Lao, 1982) and by Zenon (1983).

The Environment Canada study reported on the analysis of 13 fly ash and bottom ash samples from eight Canadian power generating stations (Sundance, Grand Lake, Boundary Dam, Lakeview, Nanticoke, Lambton, Lakeview, and Hearn). Analyses were conducted for tetrachloro- to octachlorodioxins and -furans using negative oxygen ions in chemical ionization GC/MS detection techniques. The overall detection limit for the complete method was reported as being approximately 0.050 ng/g.

The 1983 study by Zenon and Section A of this study have dealt with the analysis of 45 PCF ash samples (39 fly ash and 6 bed ash samples) along with 3 AFBC ash samples. Detection limits ranged from 0.0001 to 0.040 ng/g for octachloro to tetrachloro congeners. Samples from Sundance, Boundary Dam, Nanticoke, and Lambton were also among those analyzed. (Collections were made at times different from those of EPS samples).

In these studies, fly ash and bottom ash samples from PCF power generating stations were found to contain very low or undetectable levels of tetra- to octachlorodioxins. Some low concentrations of pentachloro- and hexachlorodioxins were reported in the later studies, most of which would not have been detectable in the earlier Environment Canada study. In the analysis for PCDF, the Environment Canada study reported no detectable levels, whereas in the later studies, pentachloro- and hexachlorofurans were detected at levels usually within 0.01 to 0.03 ng/g; but in some cases, for example P_5CDF, the levels were as high as 2.8 ng/g. It is difficult to compare the data of these studies directly because of a difference in methodology. Given that some samples were from the same power plants, they were, however, collected at different times, prepared by different laboratories, and quantitated according to different standards. Large variations are known to occur between ash samples collected from a single source at different times (NRC, 1981), and significant differences are known to occur between dioxin/furan standards in different laboratories (Zenon, 1983).

A general conclusion can be deduced from these studies on the PCDD/PCDF concentrations in PCF ashes. Concentrations of PCDD/PCDF are considerably lower in these PCF ashes than in ESP ashes from municipal incinerators. PCDD concentrations in ashes from 25 municipal incinerators in Europe (NRC, 1981) average 54 to 326 ng/g for summed concentrations within the tetrachloro to octachloro homologues. Compared to

the average (undetected values) of approximately 0.020 ng/g in the PCF ashes, the PCDD concentrations range from 3 to 4 orders of magnitude lower in concentration than their concentrations in municipal incinerator ashes. The data on PCDF are less abundant but also indicate a range of 1 to 3 orders of magnitude lower in concentration in PCF ashes than in municipal incinerator ashes.

10 TOTAL EXTRACTABLE ORGANIC HALOGEN

The analysis of total extractable organic halogen (TEOX) in combustion feeds, ashes, and emissions was proposed by Haile (1983) as a surrogate parameter for cost-effective screening. The procedure used in the U.S. study involved benzene soxhlet extraction of fly ash followed by three water washes of the extract, solvent evaporation until just dry and addition of 200 µL of benzene in preparation for short-column GC/Hall detector analysis. A similar approach was used in this study for the analysis of TEOX in fly ash samples from PCF power generating stations. Samples were extracted with toluene soxhlet. A portion equivalent to 4 g of the extract was evaporated to 1.0 mL and analyzed with a Dohrmann MCTS-20 microcoulometer.

Two differences exist between these approaches. In this study, the solvent extract was not washed with water, and final solvent volumes were not taken below 1.0 mL. The water-washing step was not incorporated to eliminate possible losses of such water-soluble chlorinated organics as chlorophenols, which are known to be present in many municipal incinerator ashes. Also, solvent extracts were not taken to complete dryness to minimize the losses of the more volatile chlorinated organics such as chlorinated benzenes.

The results of the analysis of PCF fly ashes from Poplar River, Battle River, and Lingan are recorded in Table 10-1, as are the TEOX results on the National Bureau of Standards' standard reference material of urban dust.

TABLE 10-1 SUMMARY OF TOTAL EXTRACTABLE ORGANIC HALOGEN IN FLY ASH SAMPLES FROM PCF POWER GENERATING STATION

Power Station	No. of Samples	No. of Detections	Concentration (µg/g)	Mean Concentration (µg/g)
Poplar River	1	1	5.25	5.25
Battle River	13	9	<0.02 - 5.42	0.9
Lingan	8	8	0.55 - 14.81	4.28
Urban Dust SRM	2	2	1308 - 1457	1382

Comparison of the data from Battle River and Lingan shows a lower mean concentration and frequency of detection of TEOX in the Battle River ESP ashes. Also the reference material of urban dust contained significantly higher concentrations of TEOX (300 to 1500 times higher) than the PCF ashes.

Linear regression analysis of the TEOX data from Battle River and Lingan revealed a significant correlation between TEOX concentrations in the ESP ashes and the location of the ESP bank from which the ash was collected. This suggests a correlation with the particle size distribution and surface area of the collected ashes.

The results of the TEOX analyses by the Midwest Research Institute (Haile, 1983) on ash samples from the co-fired power plant were lower than those listed in Table 10-1. The concentrations reported ranged from <0.001 to 0.362 µg Cl/g, with an average of 0.034 µg of Cl/g.

These lower values may reflect actual concentration differences between the ashes or between particle capture efficiency, but they may also reflect the differences in sample preparation from that described under "Analytical Protocol" in Section A. Additional TEOX data for comparison are needed, as well as a standard for sample preparation to permit more valid data comparisons. An NBS reference sample of urban dust would greatly assist in these studies.

Further study is also needed to identify those chlorinated organics that contribute to the total extractable organic halogen content of these ashes. The preliminary focus of such a study should be on chlorinated phenols, chlorinated benzenes, and PCB. The study should be sufficiently sensitive to measure low ng/g concentrations of these contaminants accurately.

11 SUMMARY

The analysis of ESP-captured PCF ashes to date has revealed no extractable trace organics above the 0.5-µg/g concentration level. The presence of benzyl contaminants formed during the toluene soxhlet extraction (method-incurred) limits the identification and quantitation of contaminants at lower concentrations. Despite its somewhat lower extraction efficiency, benzene should be used in any future characterization analyses for contaminants at ng/g concentrations.

Analysis for polyaromatic hydrocarbons has shown that while significant concentrations of numerous PAH are present in stack emissions, low ppb to non-detectable concentrations are determined in PCF fly ashes using HRGC/MS analyses. Further improvement in the detection limits of PAH is possible through the use of multiple-ion detection (MID) GC/MS or high-pressure liquid chromatography analysis, if required for mass balance calculations.

Polychlorinated dibenzo-ρ-dioxins and furans have generally not been detected in PCF ashes; P_5CDF and H_6CDF have been detected at low parts-per-trillion concentrations. This is in marked contrast to the reported medium to high parts-per-billion concentrations in municipal fly ash samples. Regression analysis of the PCDD/PCDF concentration data and the TEOX concentration data shows no significant correlation.

Total extractable organic halogen concentrations have been found to average between 0.9 to 5.25 µg Cl/g in ESP fly ash samples from the Battle River, Lingan, and Poplar River power generating stations. Further data are necessary for comparison with other combustion ashes and for identification of those chlorinated organics present at parts-per-billion (ng/g) concentrations that make up the measured TEOX.

Significant correlations have been indicated between the ash TEOX concentration and the point of sample collection within the ESP bank. The highest TEOX concentrations occurred in ashes collected from the ESP row closest to the exit of the ESP unit. Further work is necessary to determine whether TEOX concentrations correlate with particle size distributions and surface areas of the collected ashes.

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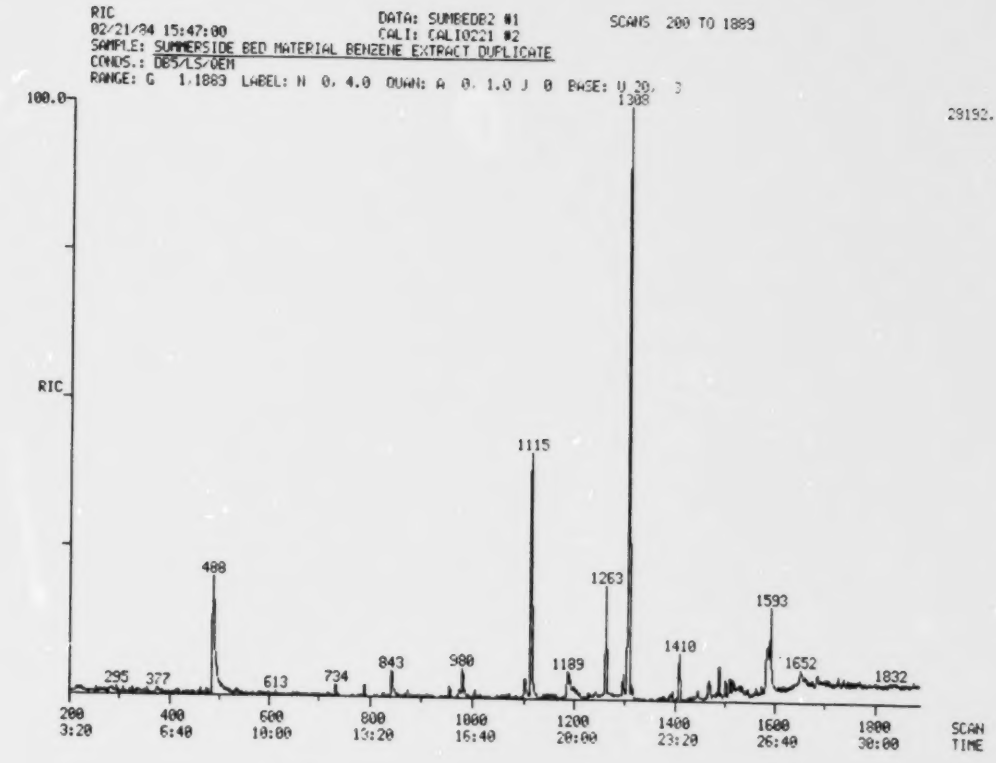
APPENDIX A

CHROMATOGRAMS AND SPECTRA FROM ASH CHARACTERIZATIONS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1115
488
1263
1593
1410
1652
1832
1189
843
980
734
613
295
377
200
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400
6:40
600
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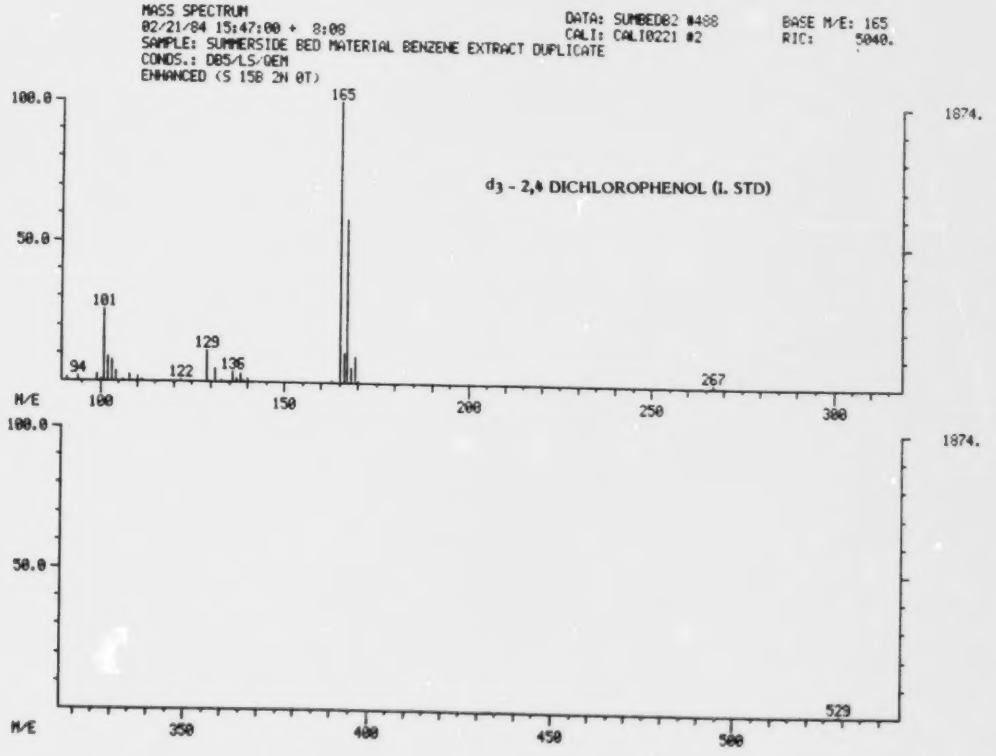
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50.0
165
1874.
d3 - 2,4 DICHLOROPHENOL (I. STD)
101
129
94
122
136
267
M/E
100
150
200
250
300
100.0
50.0
1874.
529
M/E
350
400
450
500

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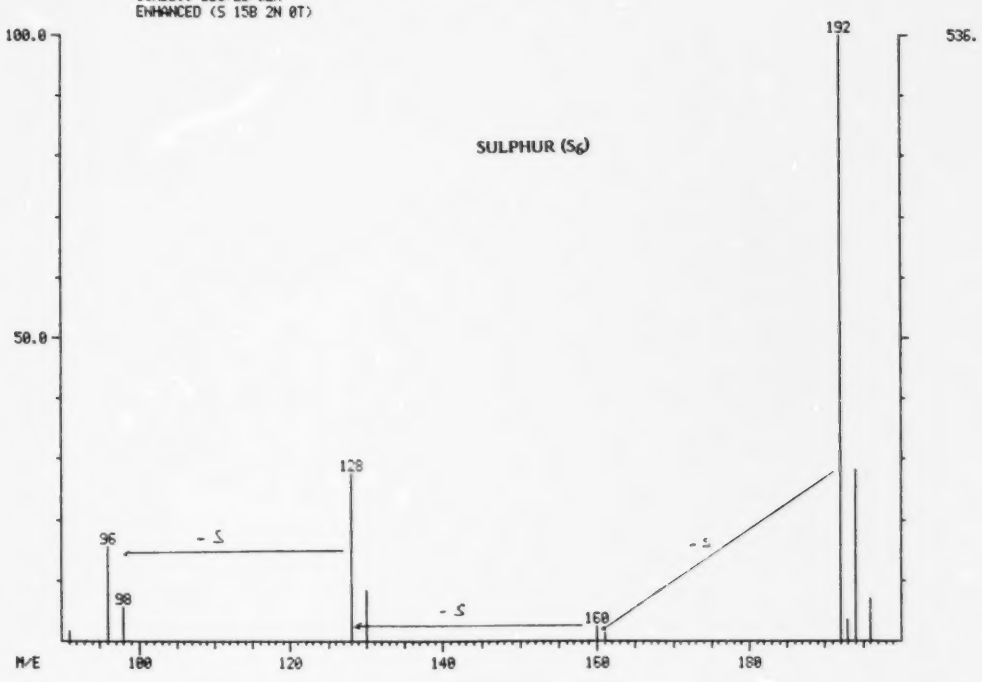

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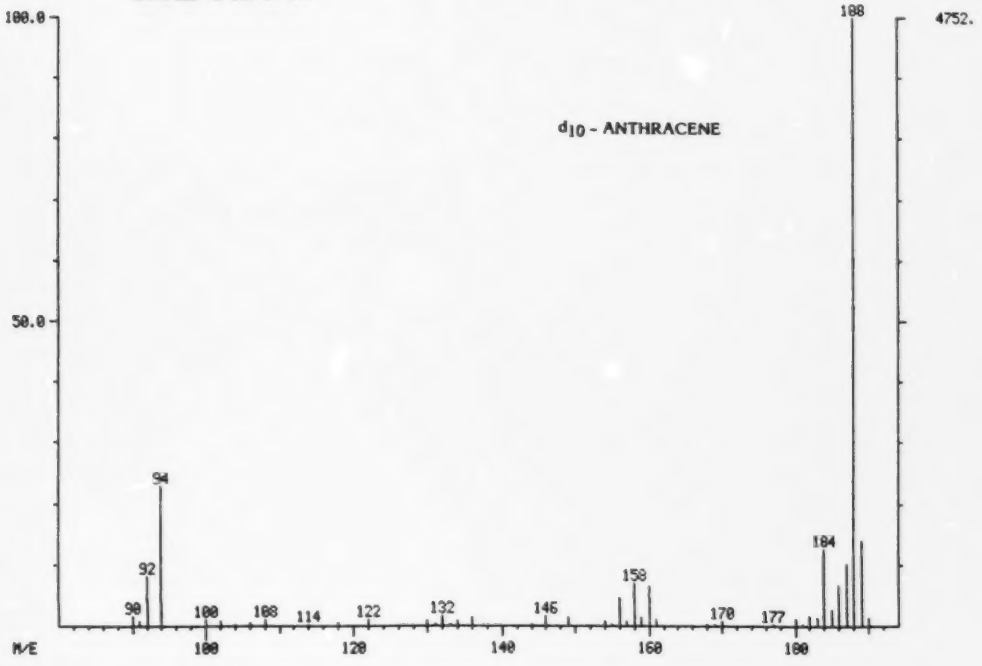

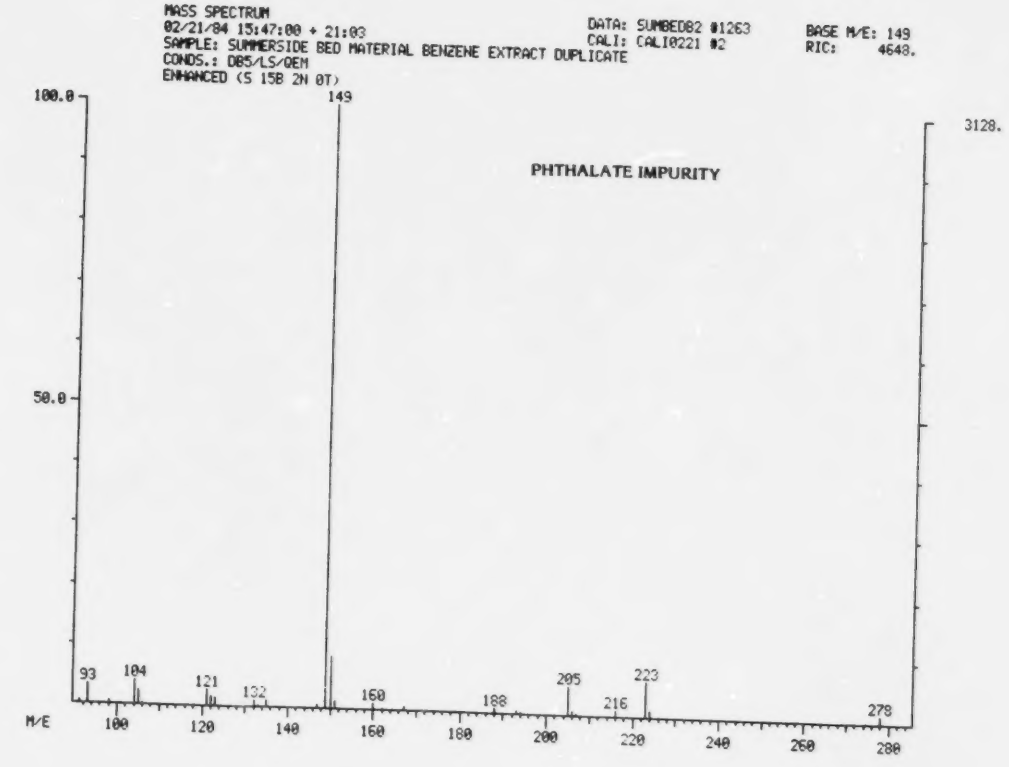
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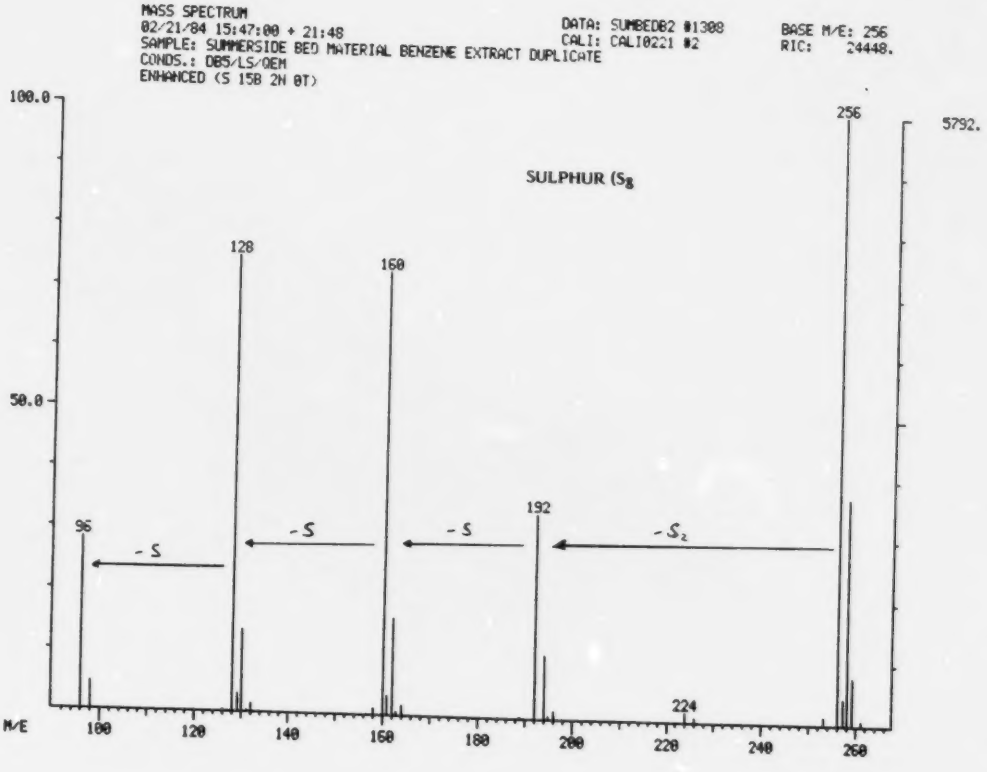
RIC: 4648.
100.0
50.0
149
3120.
PHTHALATE IMPURITY
93
104
121
132
160
188
205
216
223
278
M/E
100
120
140
160
180
200
220
240
260
280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RIC: 24448.
100.0
50.0
256
5792.
SULPHUR (S_8)
128
160
96
192
224
- S
- S
- S
- S_2
M/E
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120
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180
200
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240
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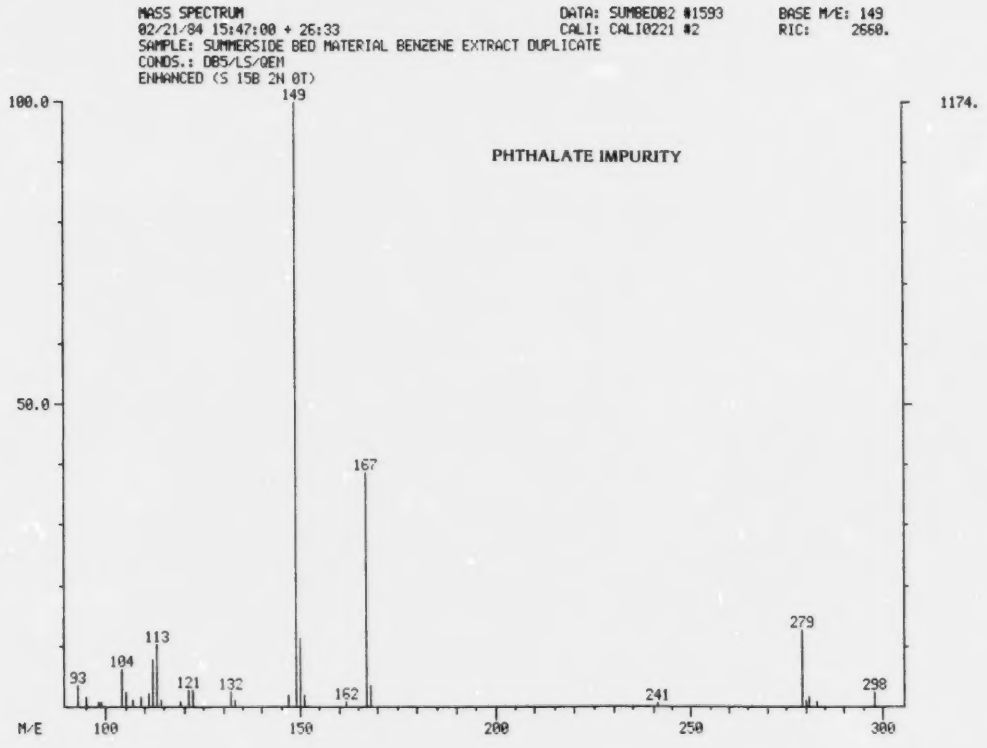
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RIC: 2660.
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1174.
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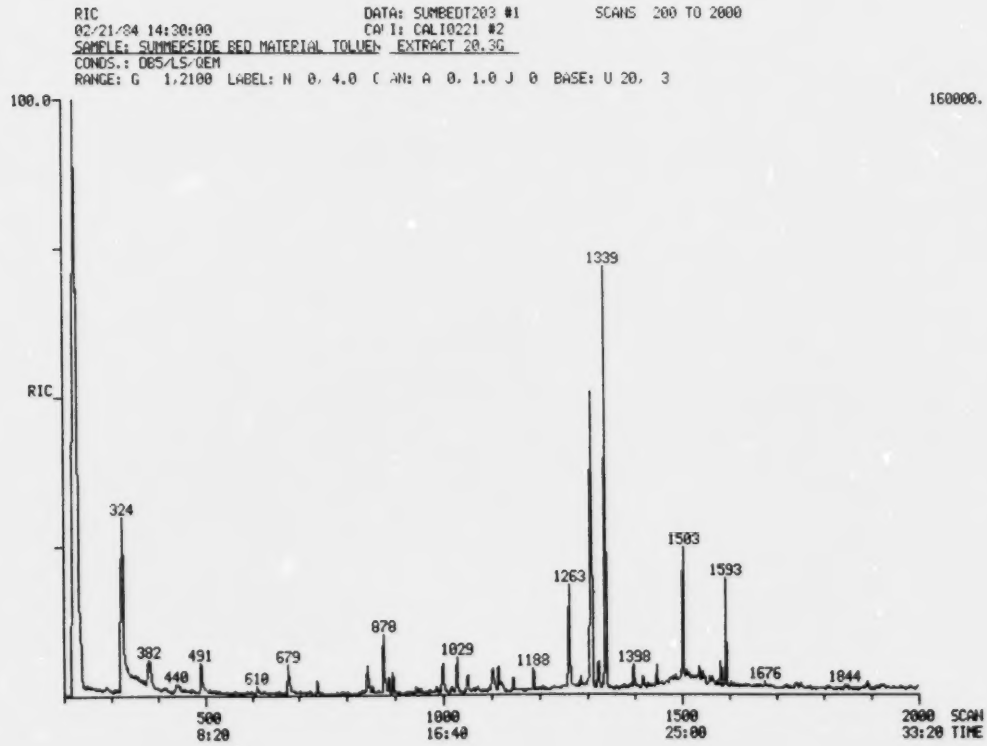
167
279
113
104
93
121
132
162
241
298
M/E
100
150
200
250
300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1503
1263
1593
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382
491
679
1029
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1844
500
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SCAN
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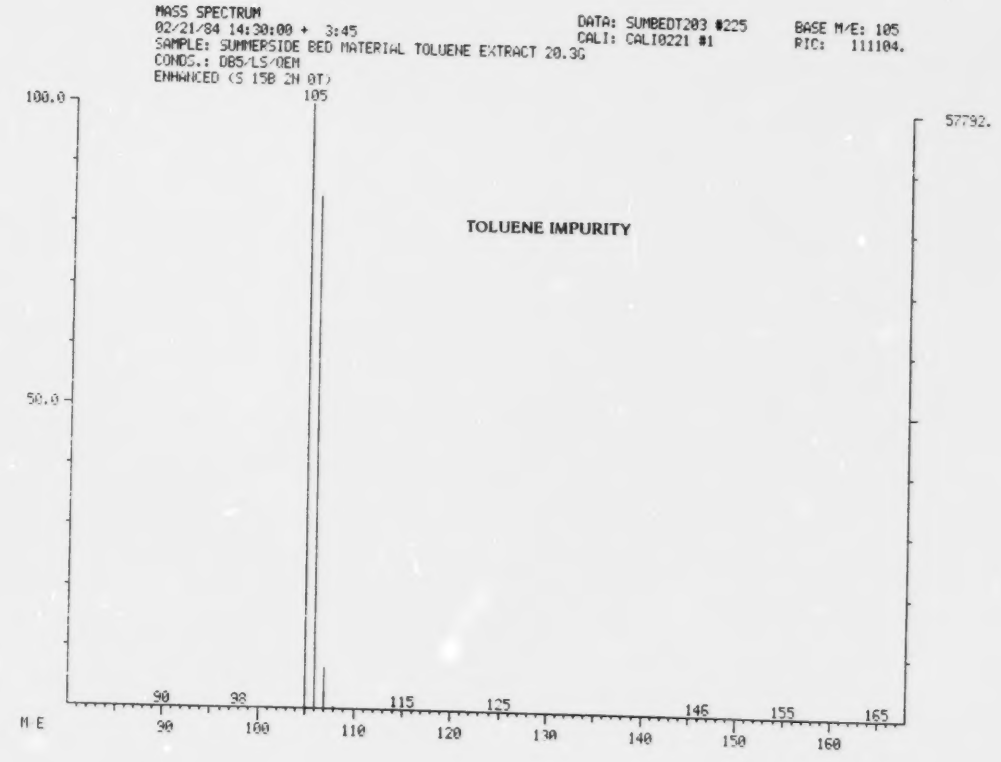
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RIC: 111104.
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105
57792.
TOLUENE IMPURITY
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125
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155
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M/E
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120
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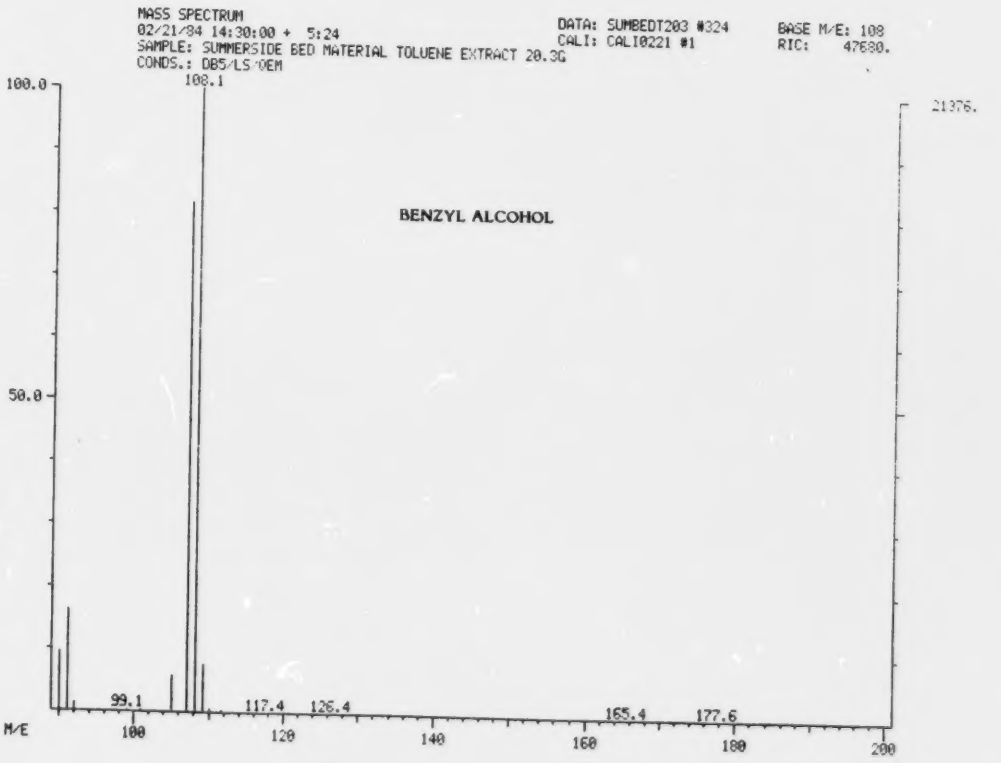
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CALI: CALI0221 #1
BASE M/E: 108
RIC: 47680.
100.0
108.1
21376.
BENZYL ALCOHOL
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177.6
M/E
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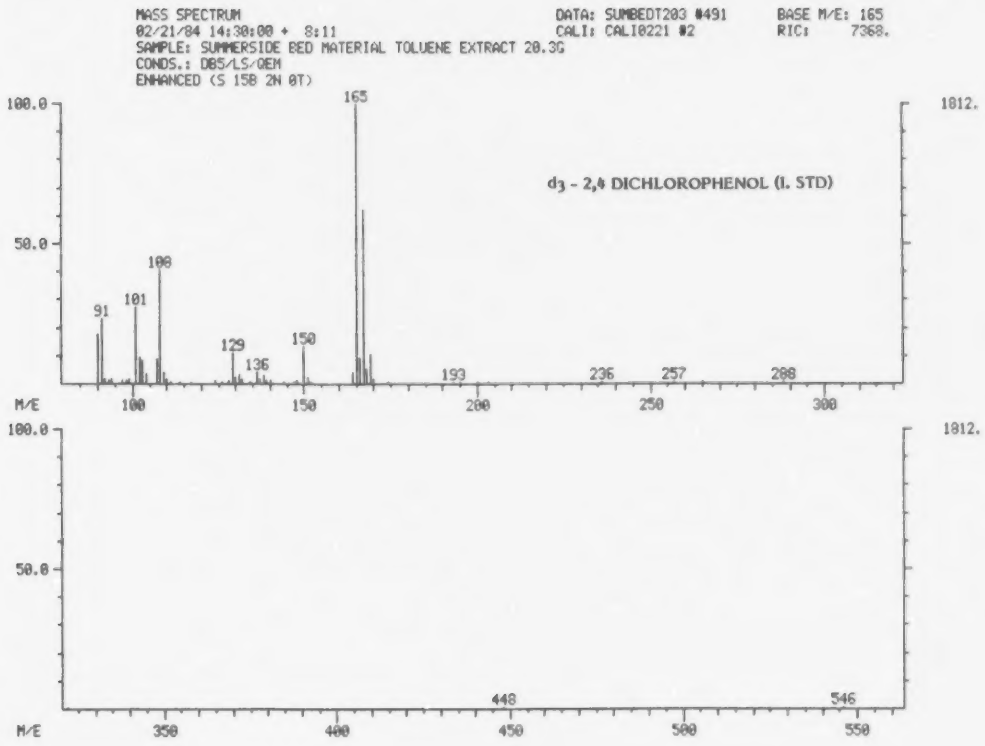
140
160
180
200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RIC: 7368.
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M/E
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165
108
101
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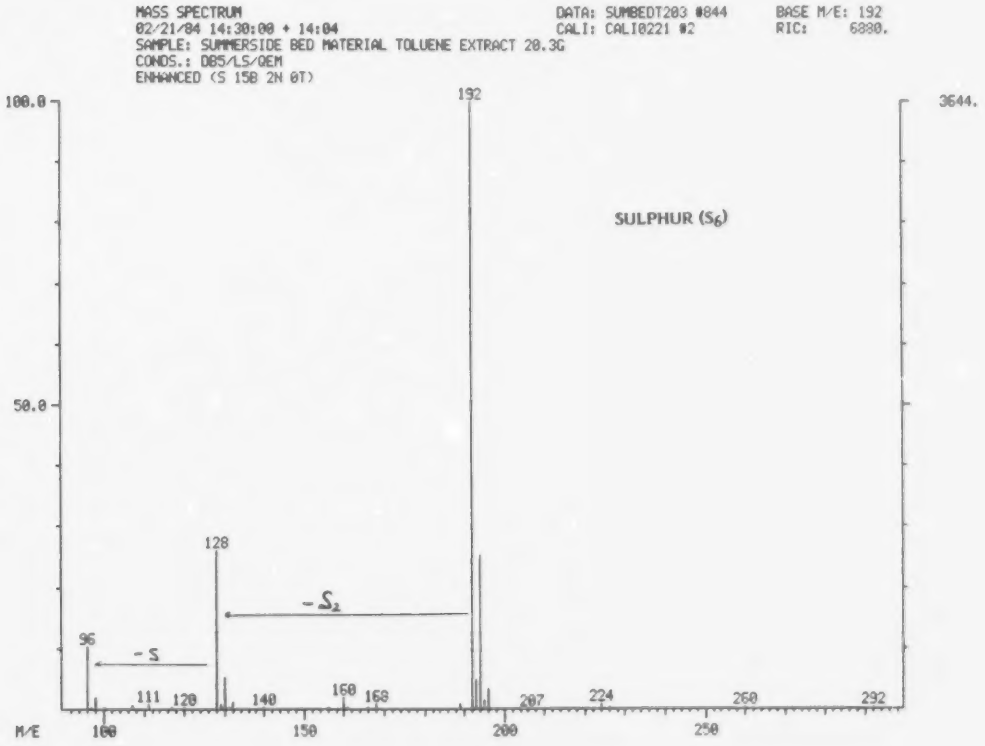
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50.0
M/E
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- S2
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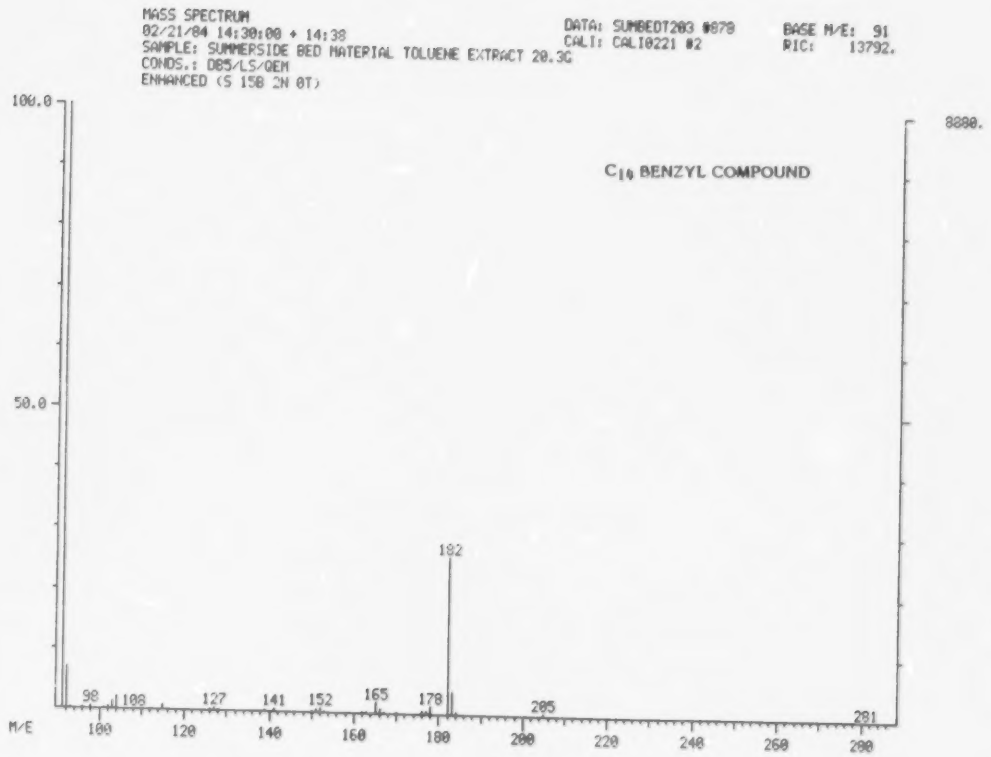
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RIC: 13792.
100.0
50.0
8880.
C14 BENZYL COMPOUND
192
90
108
127
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165
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M/E
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180
200
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260
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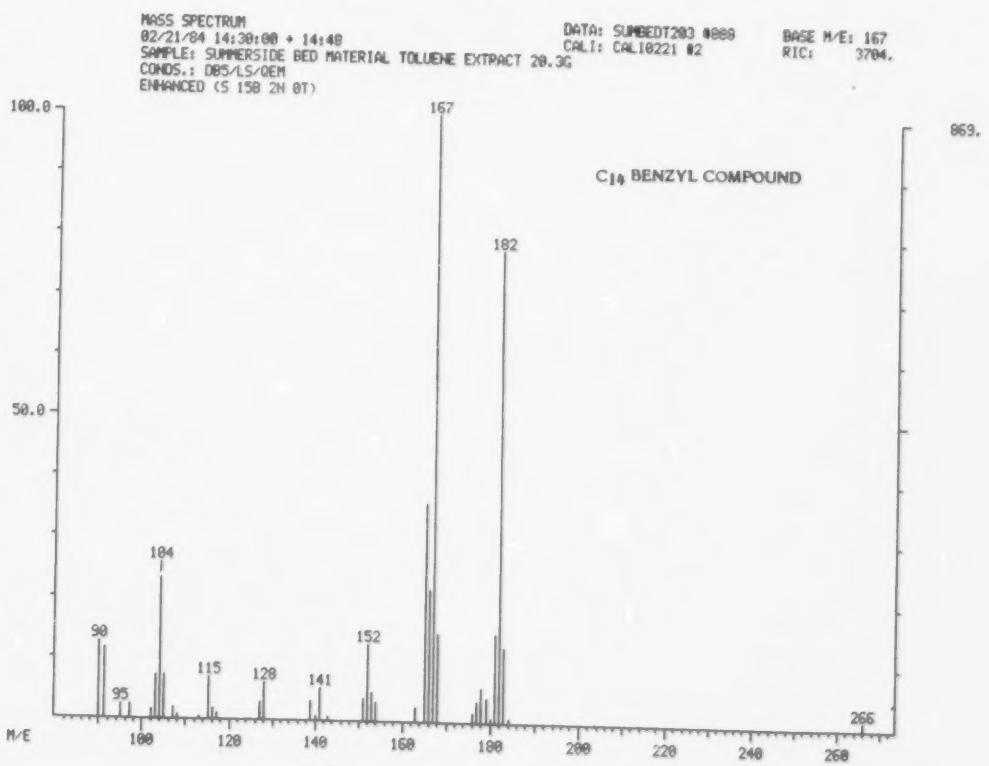
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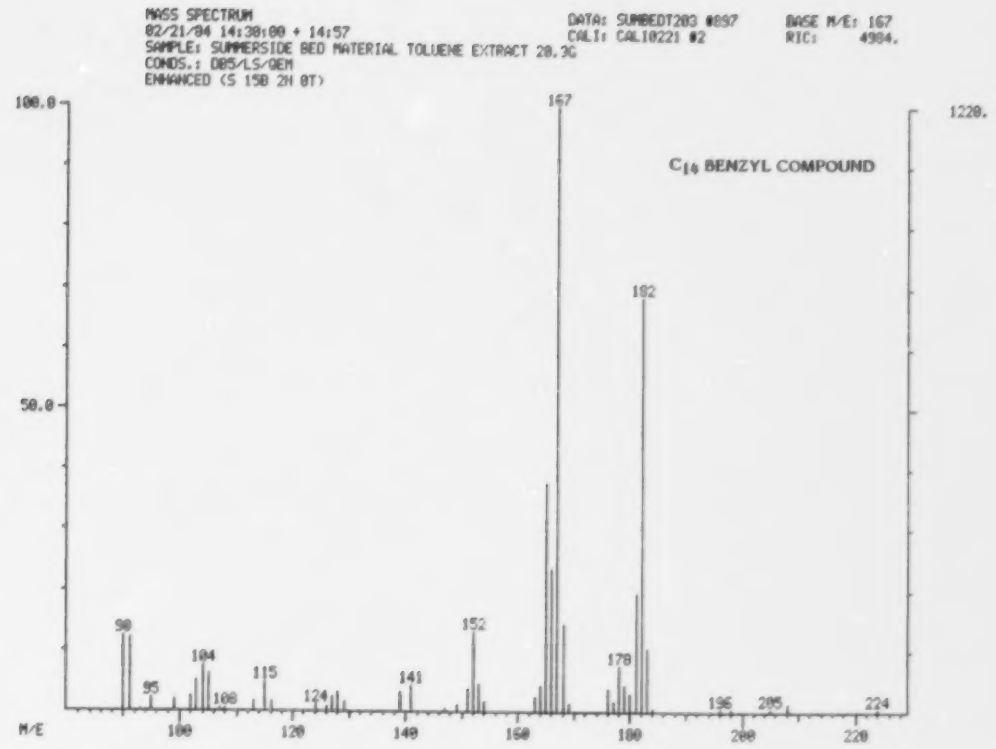
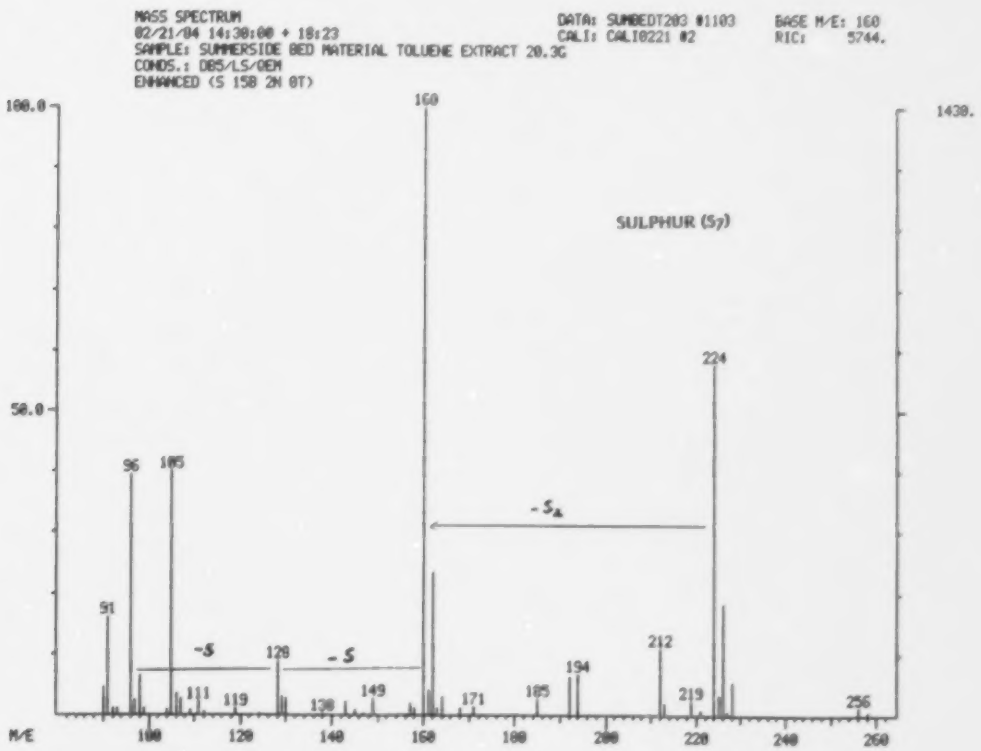
DATA: SUMBEDT203 #880
CALI: CAL10221 #2
BASE M/E: 167
RIC: 3704.
100.0
50.0
869.
C14 BENZYL COMPOUND
167
182
104
90
95
115
128
141
152
266
M/E
100
120
140
160
180
200
220
240
260

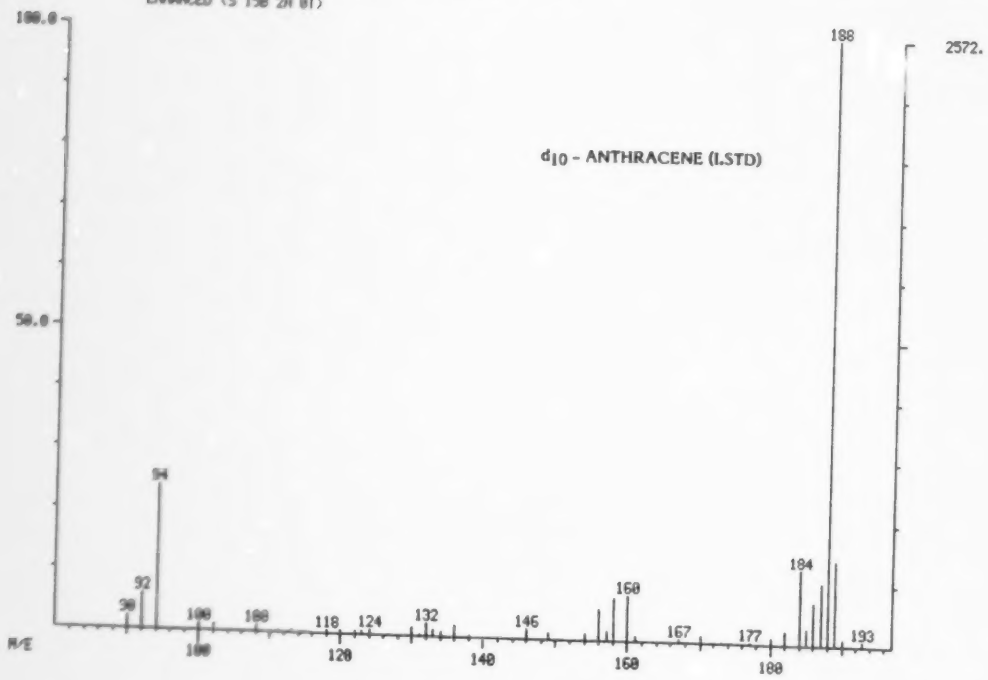

MASS SPECTRUM
02/21/84 14:30:00 + 14:57
SAMPLE: SUMMERSIDE BED MATERIAL TOLUENE EXTRACT 20.3G
CONDS.: DB5/LS/QEM
ENHANCED (S 15B 2N 0T)
DATA: SUMBEDT203 #897
CALI: CAL10221 #2
BASE M/E: 167
RIC: 4904.
100.0
50.0
1220.
167
192
C16 BENZYL COMPOUND
90
104
115
152
178
141
95
108
124
196
205
224
M/E
100
120
140
160
180
200
220


MASS SPECTRUM
02/21/84 14:30:00 + 18:23
SAMPLE: SUMMERSIDE BED MATERIAL TOLUENE EXTRACT 20.3G
CONDS.: DB5/LS/QEM
ENHANCED (S 15B 2N 0T)
DATA: SUMBEDT203 #1103
CALI: CAL10221 #2
BASE M/E: 160
RIC: 5744.
100.0
50.0
1439.
160
SULPHUR (S7)
224
96
105
-S4
91
-S
128
-S
212
194
111
119
149
171
185
219
256
M/E
100
120
140
160
180
200
220
240
260

MASS SPECTRUM
02/21/84 14:30:00 + 18:35
SAMPLE: SUMMERSIDE BED MATERIAL TOLUENE EXTRACT 20.3G
COMDS.: DB5/LS/QEM
ENHANCED (S 15B 2H 0T)

DATA: SUMBEDT203 #1115
CALI: CALI0221 #2

BASE M/E: 188
RIC: 5824.

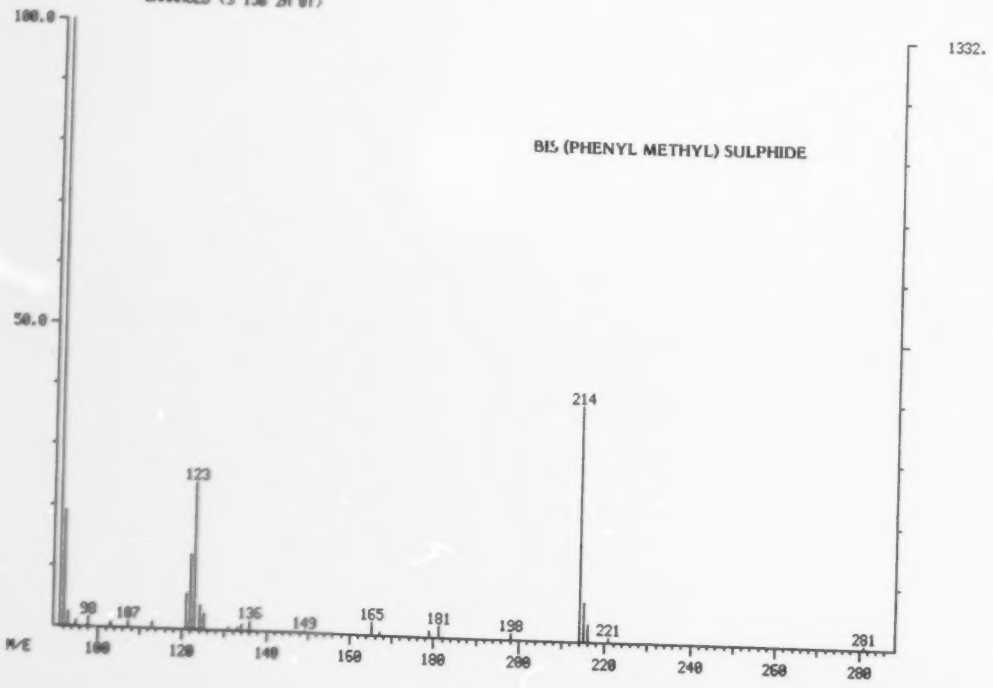


d_{10} - ANTHRACENE (I.STD)

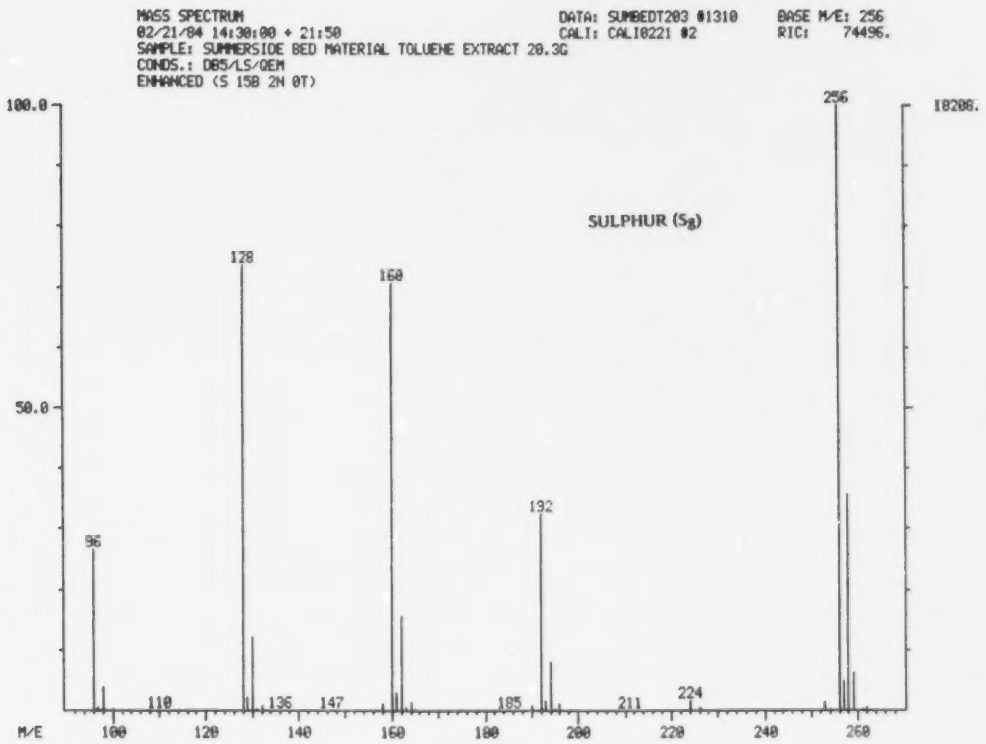
MASS SPECTRUM
02/21/84 14:30:00 + 19:05
SAMPLE: SUMMERSIDE BED MATERIAL TOLUENE EXTRACT 20.3G
COMDS.: DB5/LS/QEM
ENHANCED (S 15B 2H 0T)

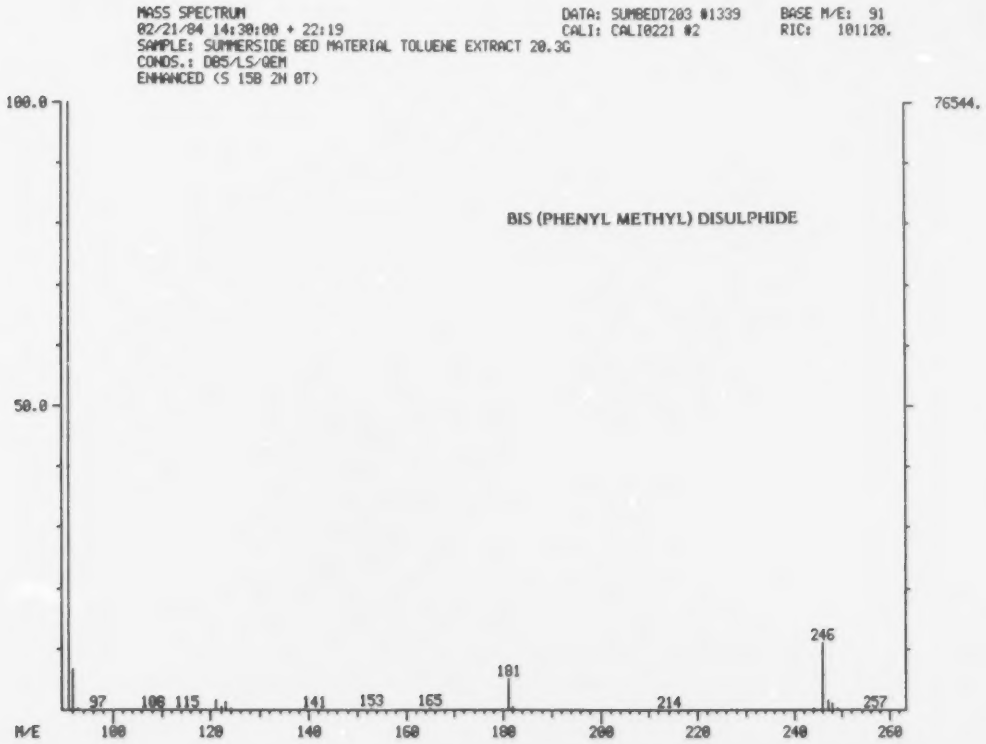
DATA: SUMBEDT203 #1145
CALI: CALI0221 #2

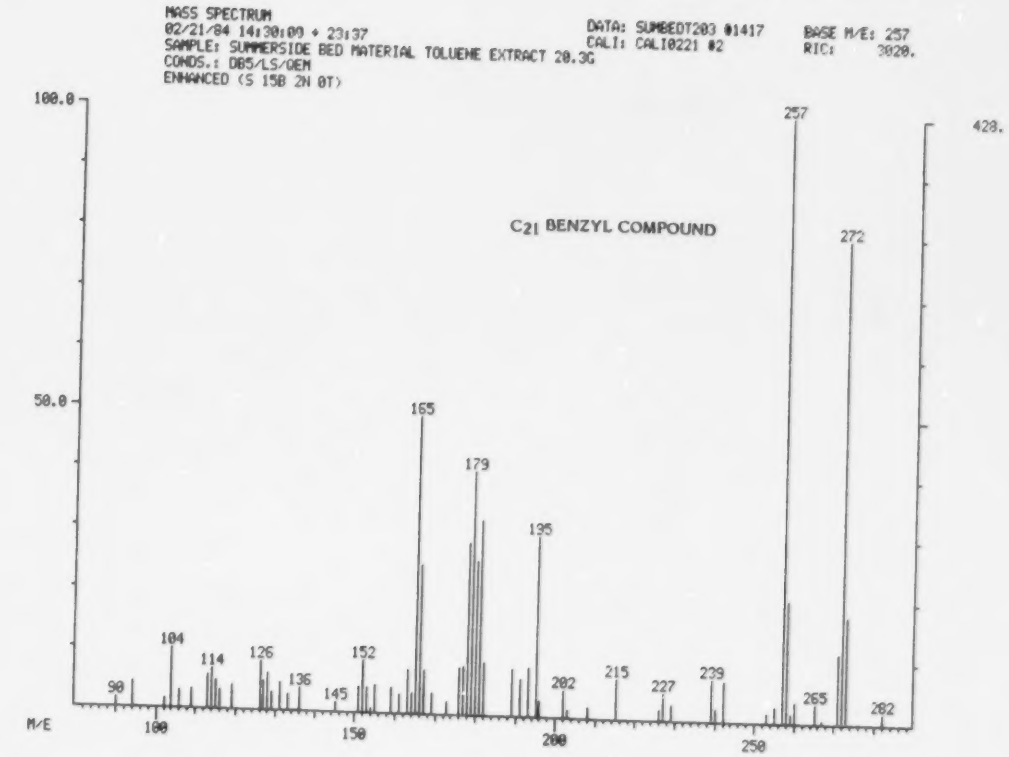
BASE M/E: 91
RIC: 3156.

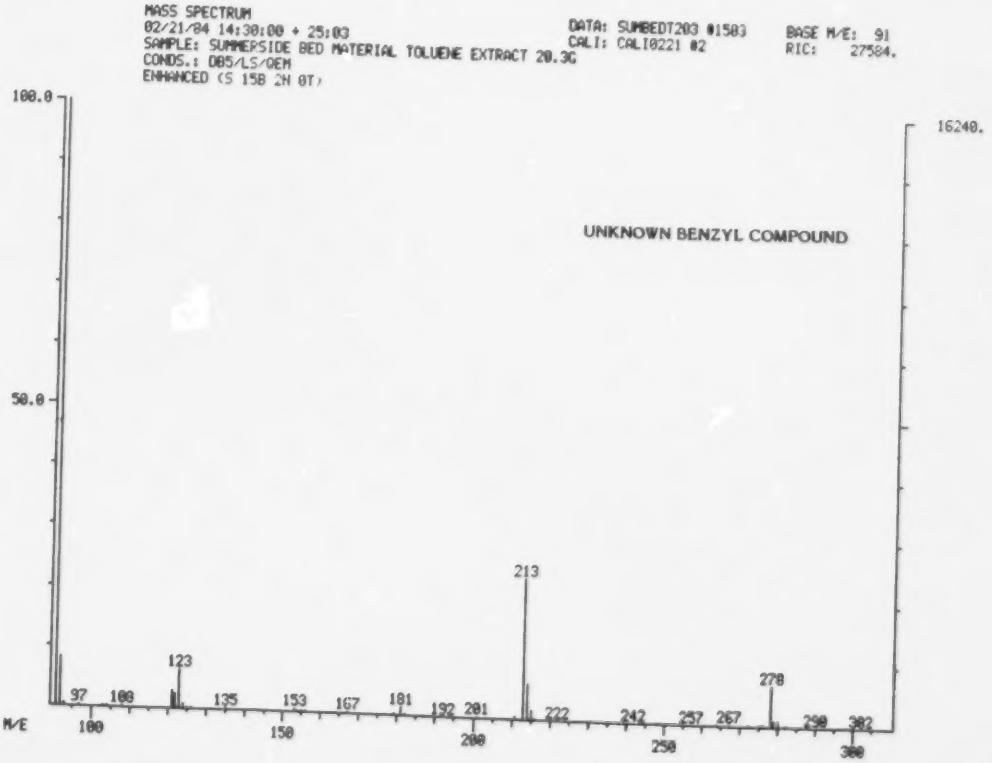


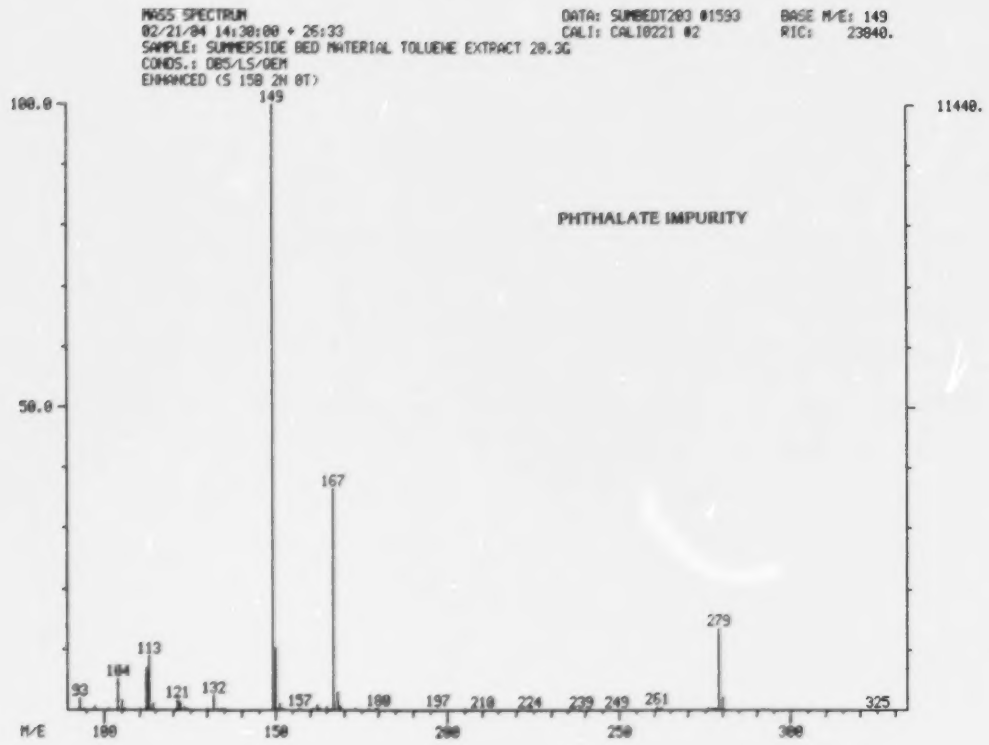
BIS (PHENYL METHYL) SULPHIDE

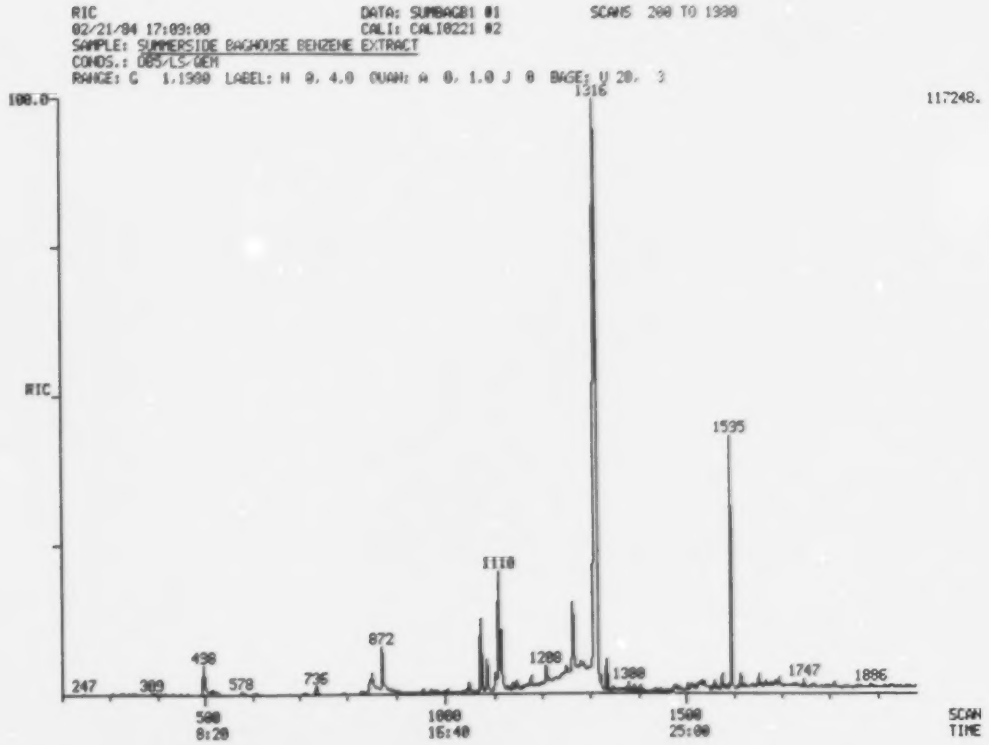

MASS SPECTRUM
02/21/84 14:30:00 + 21:50
SAMPLE: SUMMERSIDE BED MATERIAL TOLUENE EXTRACT 20.3G
CONDS.: DB5/LS/QEM
ENHANCED (S 15B 2N 0T)
DATA: SUMBEDT203 #1310
CALI: CAL10221 #2
BASE M/E: 256
RIC: 74496.
100.0
50.0
M/E
SULPHUR (S8)
256
18208.
128
160
192
96
110
136
147
185
211
224
100
120
140
160
180
200
220
240
260

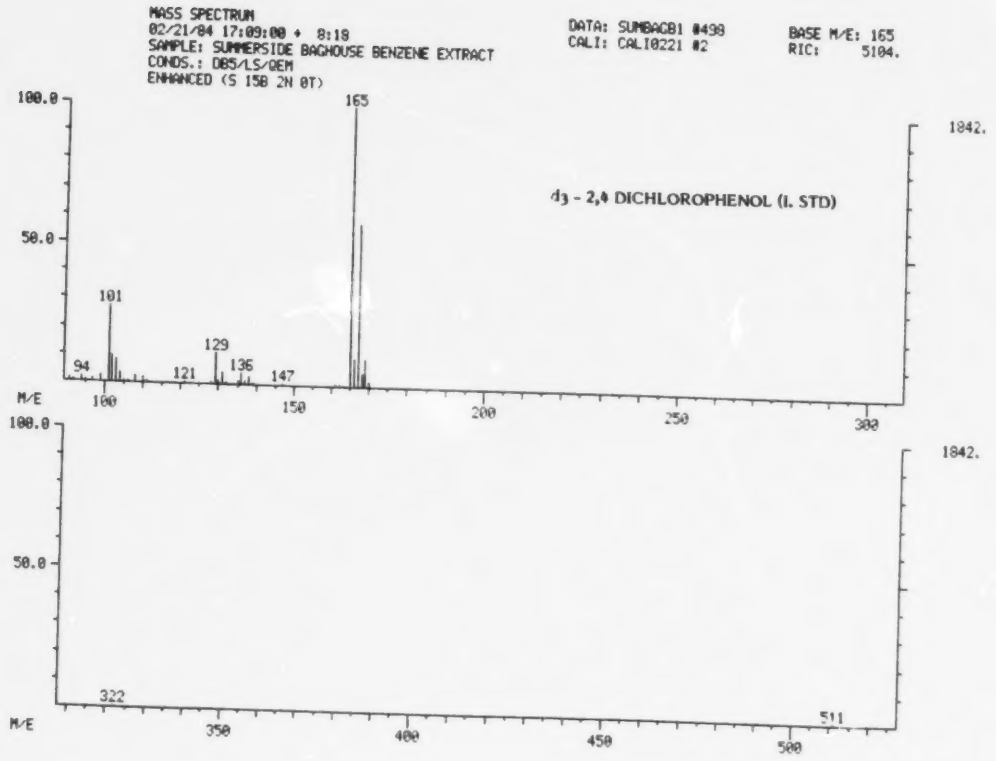

MASS SPECTRUM
02/21/84 14:30:00 + 22:19
SAMPLE: SUMMERSIDE BED MATERIAL TOLUENE EXTRACT 20.3G
CONDS.: DB5/LS/QEM
ENHANCED (S 15B 2N 0T)
DATA: SUMBEDT203 #1339
CALI: CAL10221 #2
BASE M/E: 91
RIC: 101120.
100.0
50.0
M/E
BIS (PHENYL METHYL) DISULPHIDE
76544.
246
181
97
108
115
141
153
165
214
257
100
120
140
160
180
200
220
240
260

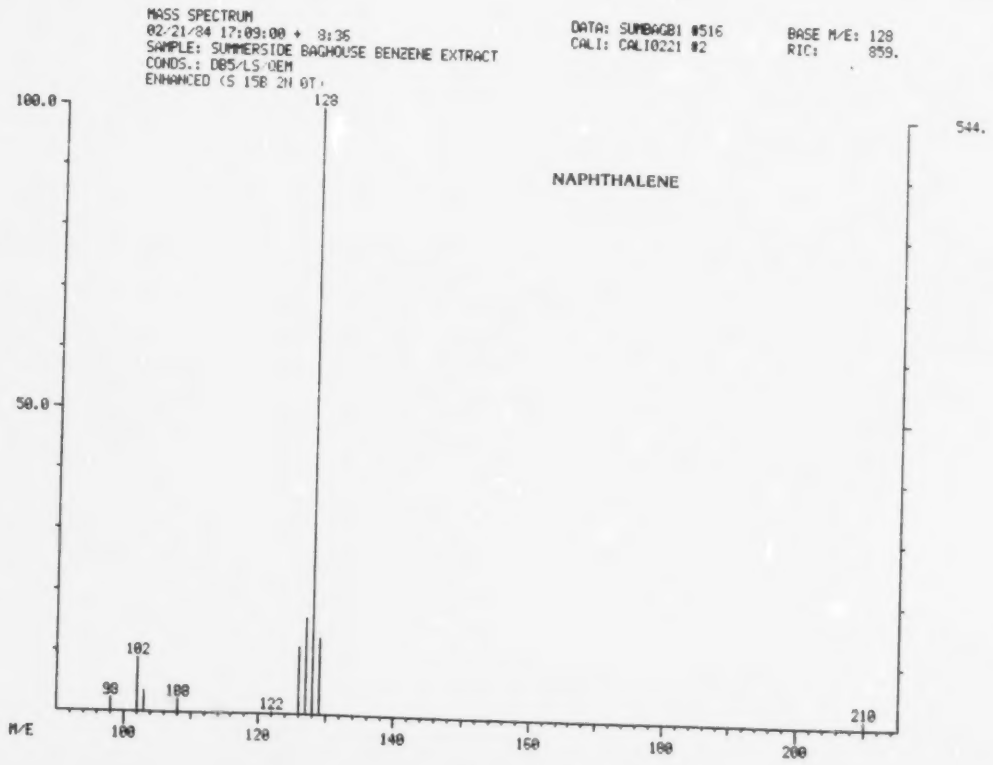

MASS SPECTRUM
02/21/84 14:30:00 + 23:37
SAMPLE: SUMMERSIDE BED MATERIAL TOLUENE EXTRACT 20.3G
CONDS.: DB5/LS/OEM
ENHANCED (S 15B 2N 0T)
DATA: SUMBEDT203 #1417
CALI: CAL10221 #2
BASE M/E: 257
RIC: 3020.
100.0
50.0
M/E
428.
257
272
165
179
135
104
114
126
152
136
145
202
215
227
239
265
282
90
100
150
200
250
C21 BENZYL COMPOUND

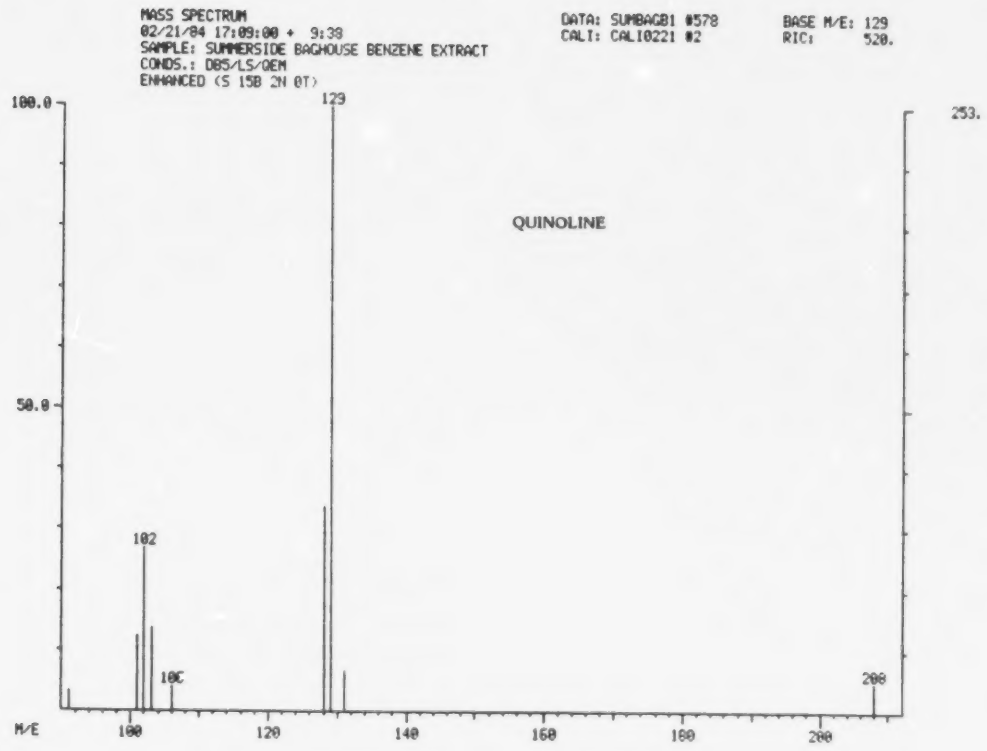

MASS SPECTRUM
02/21/84 14:30:00 + 25:03
SAMPLE: SUMMERSIDE BED MATERIAL TOLUENE EXTRACT 20.3G
CONDS.: DB5/LS/OEM
ENHANCED (S 15B 2N 0T)
DATA: SUMBEDT203 #1503
CALI: CAL10221 #2
BASE M/E: 91
RIC: 27584.
100.0
50.0
M/E
16240.
213
123
278
97
108
135
153
167
181
192
201
222
242
257
267
290
302
100
150
200
250
300
UNKNOWN BENZYL COMPOUND

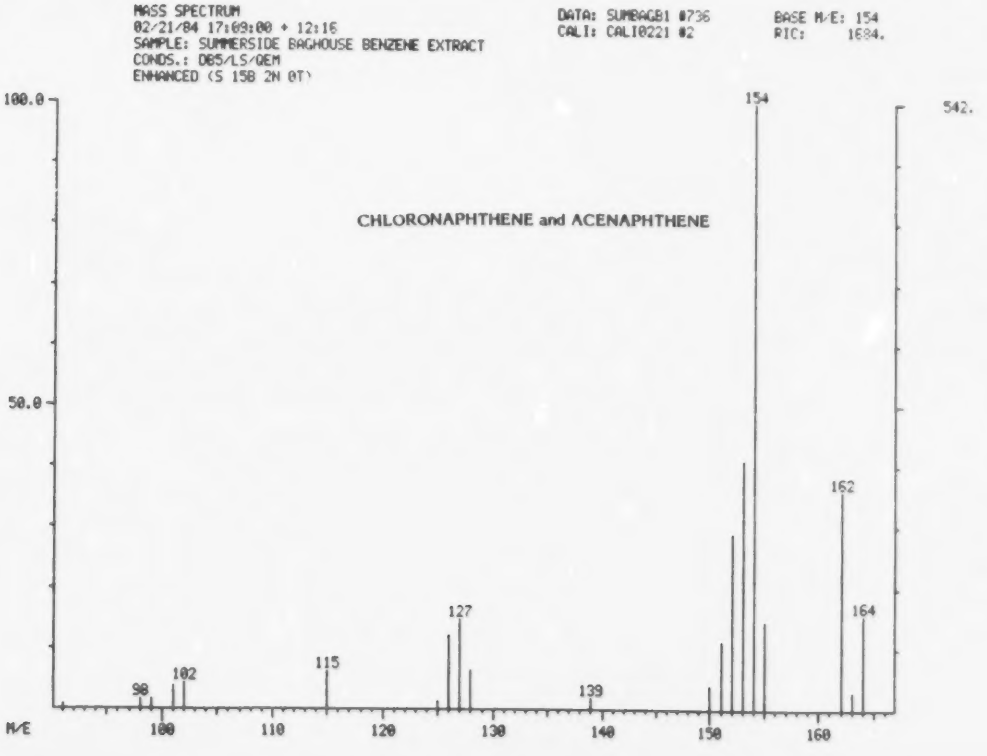

MASS SPECTRUM
02/21/84 14:30:00 + 26:33
SAMPLE: SUMMERSIDE BED MATERIAL TOLUENE EXTRACT 20.3G
CONDS.: DBS/LS/QEM
ENHANCED (S 15B 2N 0T)
DATA: SUMBEDT203 #1593
CALI: CALI0221 #2
BASE M/E: 149
RIC: 23840.
100.0
50.0
149
167
113
104
93
121
132
157
180
197
210
224
239
249
261
279
325
11440.
PHTHALATE IMPURITY
M/E
100
150
200
250
300

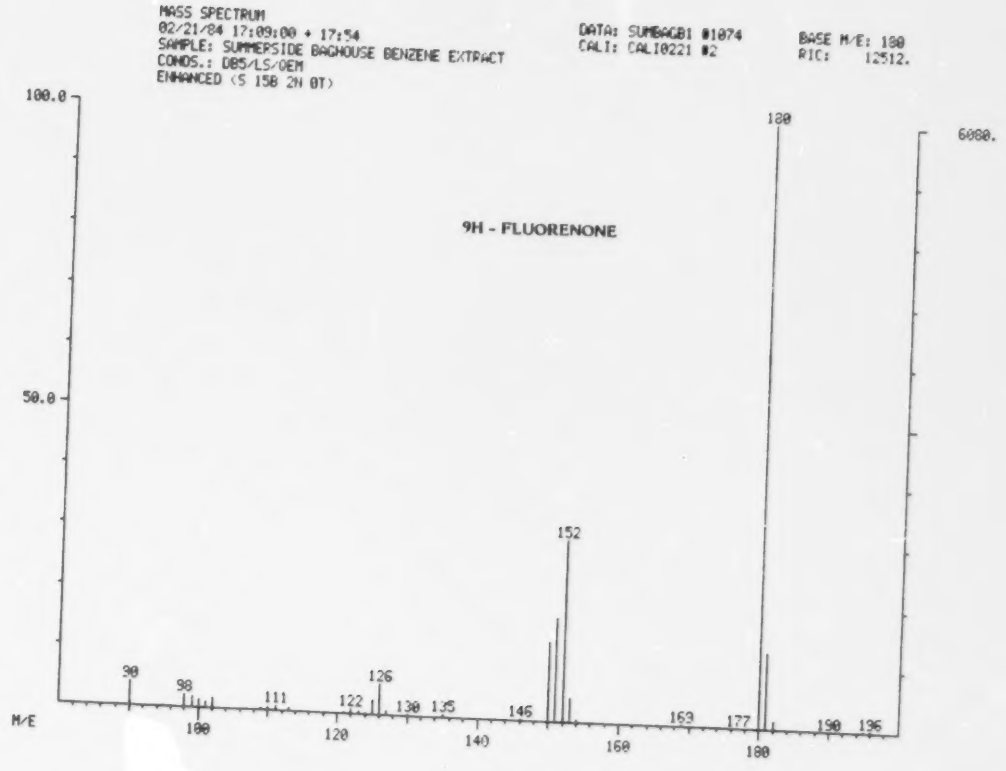

RIC
02/21/84 17:09:00
SAMPLE: SUMMERSIDE BAGHOUSE BENZENE EXTRACT
CONDS.: DBS/LS/QEM
RANGE: G 1.1500 LABEL: H 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3
DATA: SUMBAGB1 #1
CALI: CALI0221 #2
SCANS 200 TO 1930
100.0
RIC
1316
1535
1110
872
438
1288
1380
1747
1886
247
309
578
735
117248.
500
8:20
1000
16:40
1500
25:00
SCAN
TIME

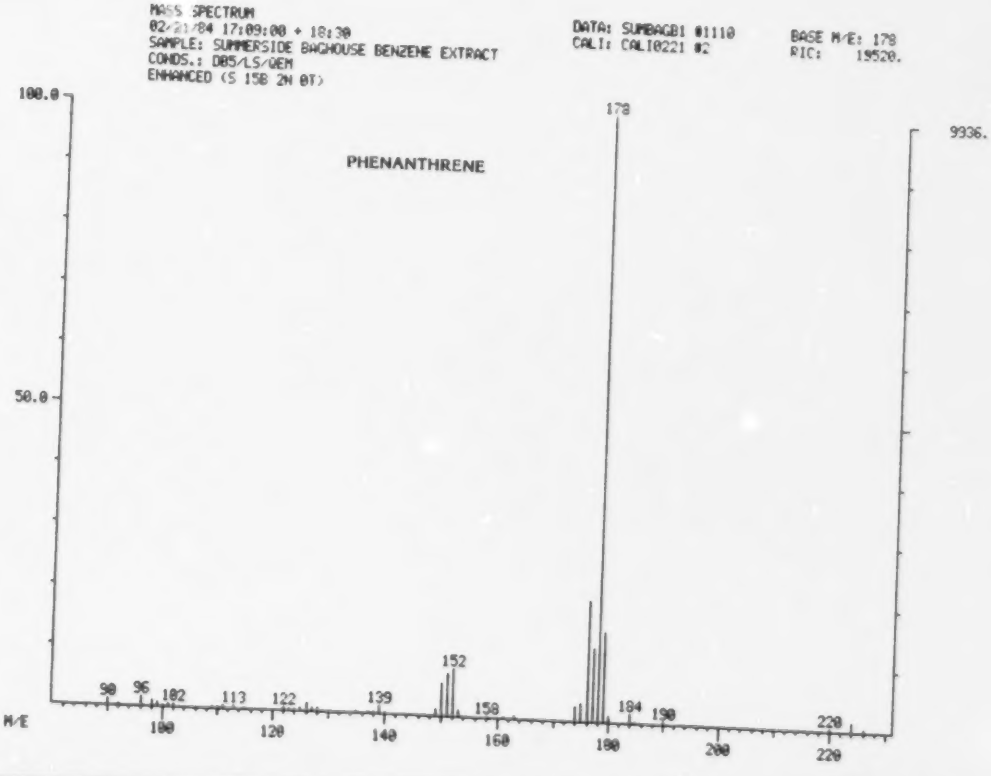

MASS SPECTRUM
02/21/84 17:09:00 + 8:18
SAMPLE: SUMMERSIDE BAGHOUSE BENZENE EXTRACT
CONDS.: DB5/LS/0EM
ENHANCED (S 15B 2N 0T)
DATA: SUMBAGB1 #498
CALI: CALI0221 #2
BASE M/E: 165
RIC: 5104.
d3 - 2,4 DICHLOROPHENOL (I. STD)
1842.
1842.
100.0
50.0
M/E
165
101
129
136
147
94
121
322
511
100
150
200
250
300
350
400
450
500

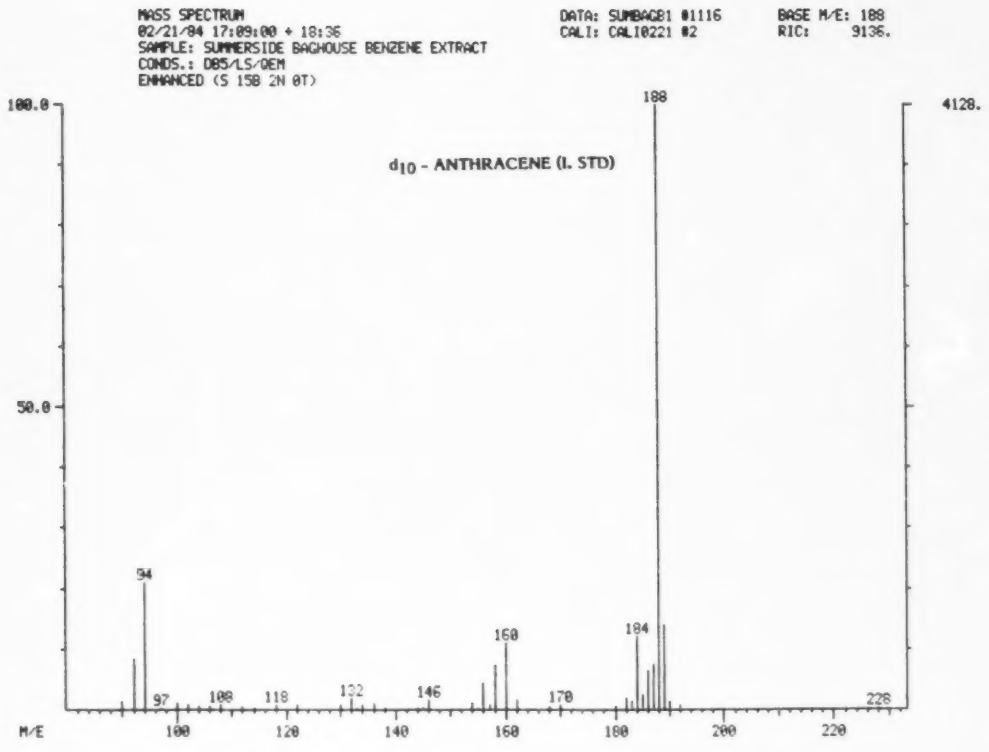

MASS SPECTRUM
02/21/84 17:09:00 + 8:36
SAMPLE: SUMMERSIDE BAGHOUSE BENZENE EXTRACT
CONDS.: DB5/LS/0EM
ENHANCED (S 15B 2N 0T)
DATA: SUMBAGB1 #516
CALI: CALI0221 #2
BASE M/E: 128
RIC: 859.
NAPHTHALENE
544.
100.0
50.0
M/E
128
102
98
100
122
210
100
120
140
160
180
200

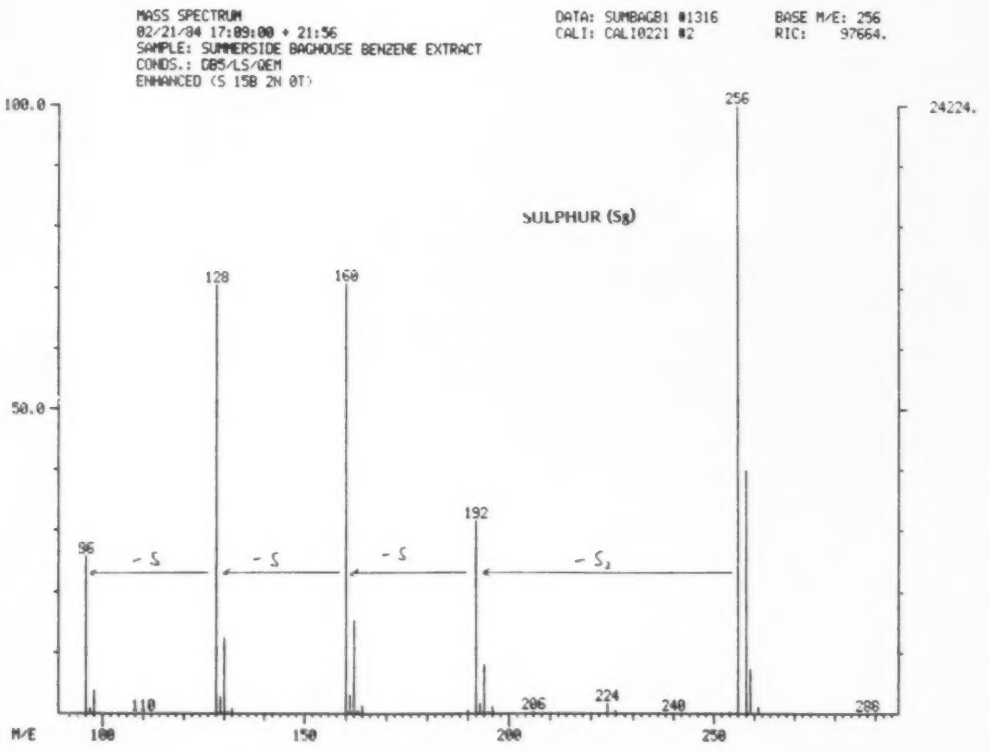

MASS SPECTRUM
02/21/84 17:09:00 + 9:38
SAMPLE: SUMMERSIDE BAGHOUSE BENZENE EXTRACT
CONDS.: DB5/LS/QEM
ENHANCED (S 15B 2N 0T)
DATA: SUMBAGB1 #578
CALI: CAL10221 #2
BASE M/E: 129
RIC: 520.
100.0
50.0
129
253.
QUINOLINE
102
103
208
M/E
100
120
140
160
180
200

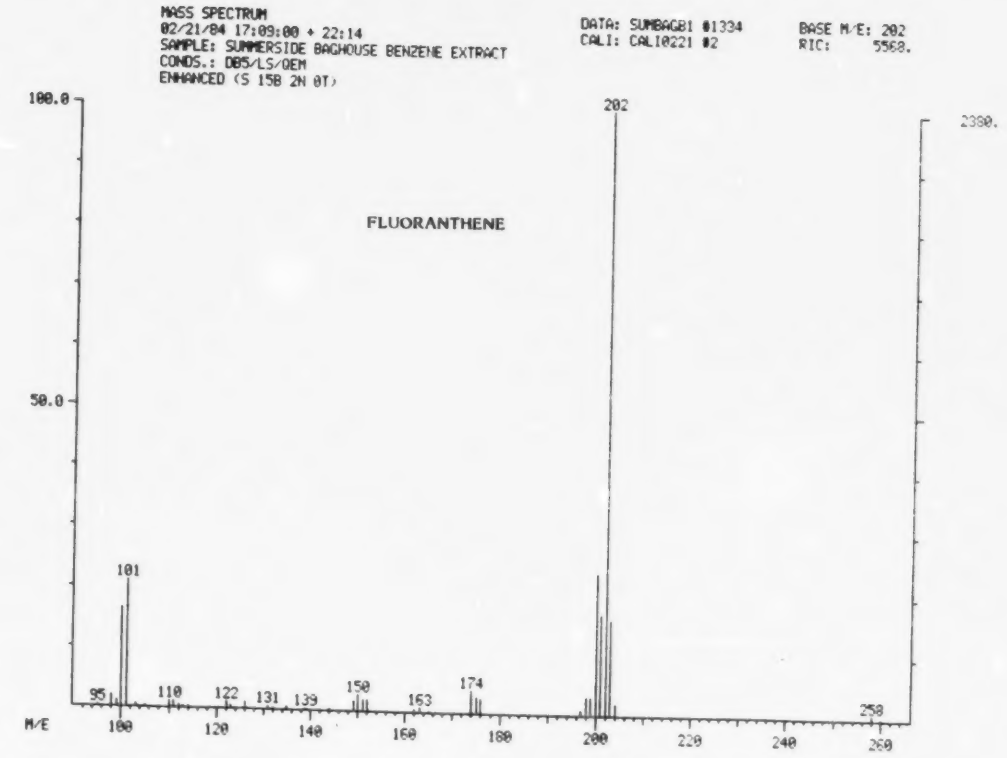

MASS SPECTRUM
02/21/84 17:09:00 + 12:16
SAMPLE: SUMMERSIDE BAGHOUSE BENZENE EXTRACT
CONDS.: DB5/LS/QEM
ENHANCED (S 15B 2N 0T)
DATA: SUMBAGB1 #736
CALI: CAL10221 #2
BASE M/E: 154
RIC: 1684.
100.0
50.0
154
542.
CHLORONAPHTHENE and ACENAPHTHENE
162
164
127
115
102
98
139
M/E
100
110
120
130
140
150
160

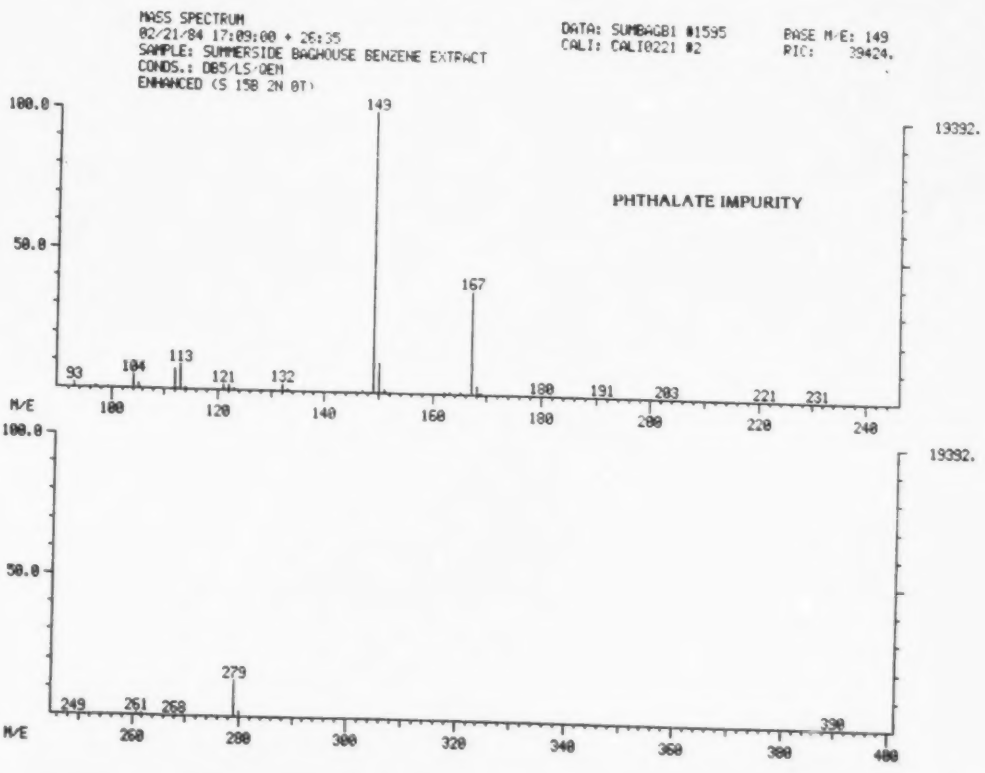

MASS SPECTRUM
02/21/84 17:09:00 + 17:54
SAMPLE: SUMMERSIDE BAGHOUSE BENZENE EXTRACT
CONDS.: DB5/LS/QEM
ENHANCED (S 15B 2N 0T)
DATA: SUMBAGB1 #1074
CALI: CALI0221 #2
BASE M/E: 180
RIC: 12512.
9H - FLUORENONE
100.0
50.0
6000.
180
152
126
90
98
111
122
130
135
146
163
177
190
196
M/E
100
120
140
160
180

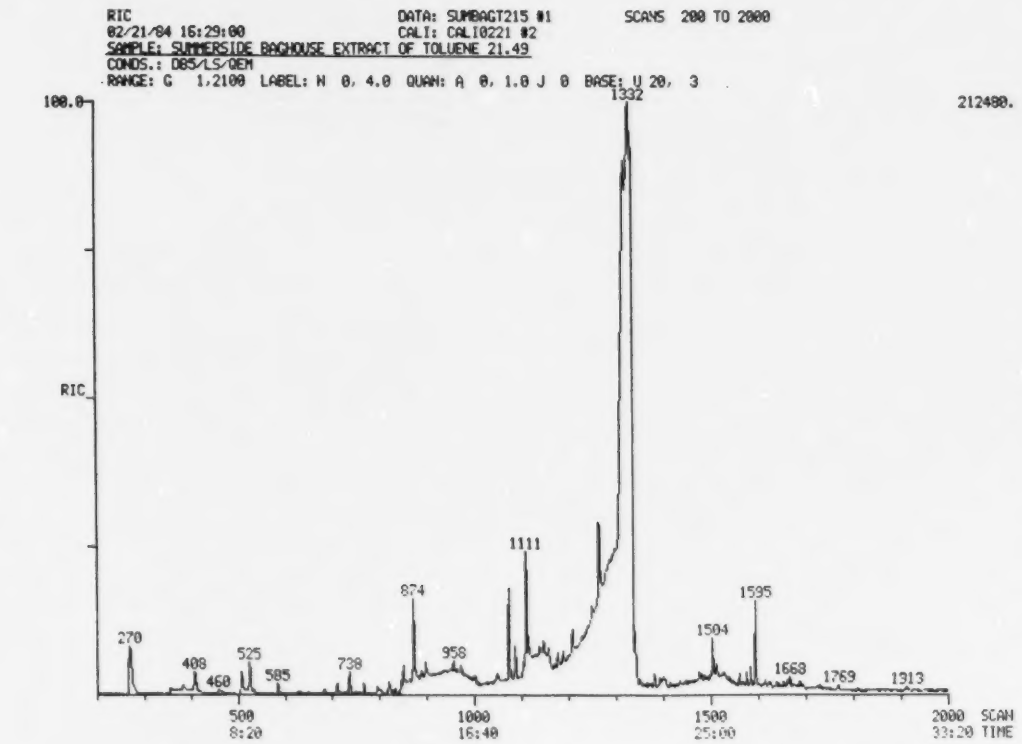

MASS SPECTRUM
02/21/84 17:09:00 + 18:30
SAMPLE: SUMMERSIDE BAGHOUSE BENZENE EXTRACT
CONDS.: DB5/LS/QEM
ENHANCED (S 15B 2N 0T)
DATA: SUMBAGB1 #1110
CALI: CALI0221 #2
BASE M/E: 178
RIC: 19520.
PHENANTHRENE
100.0
50.0
9936.
178
152
90
96
102
113
122
139
158
184
190
220
M/E
100
120
140
160
180
200
220

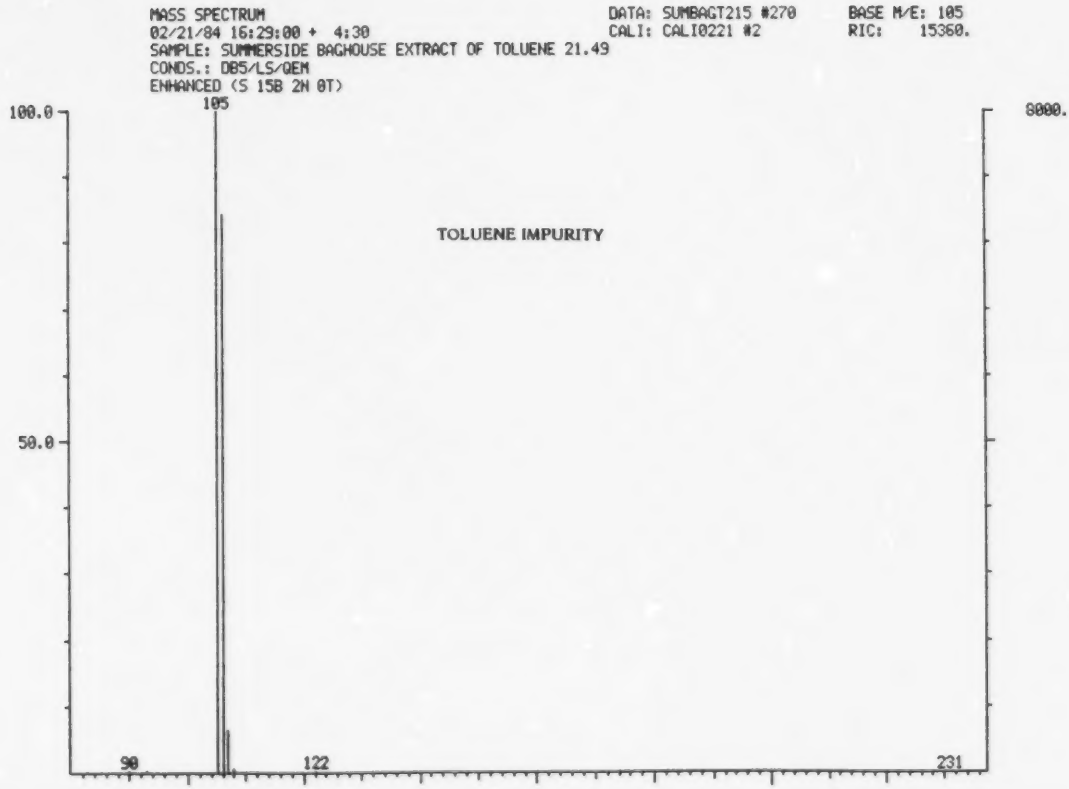

MASS SPECTRUM
02/21/84 17:09:00 + 18:36
SAMPLE: SUMMERSIDE BAGHOUSE BENZENE EXTRACT
CONDS.: DB5/LS/QEM
ENHANCED (S 15B 2N 0T)
DATA: SUMBAGB1 #1116
CALI: CAL10221 #2
BASE M/E: 188
RIC: 9136.
100.0
50.0
4128.
d_{10} - ANTHRACENE (I. STD)
188
94
160
184
97
108
118
132
146
170
228
M/E
100
120
140
160
180
200
220

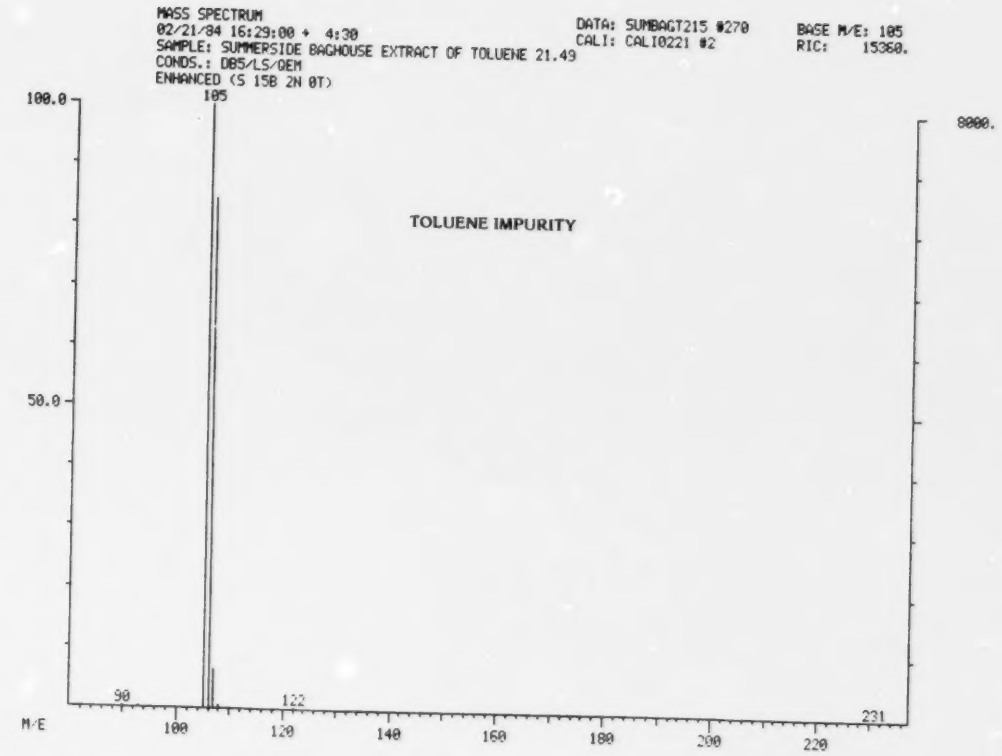

MASS SPECTRUM
02/21/84 17:09:00 + 21:56
SAMPLE: SUMMERSIDE BAGHOUSE BENZENE EXTRACT
CONDS.: DB5/LS/QEM
ENHANCED (S 15B 2N 0T)
DATA: SUMBAGB1 #1316
CALI: CAL10221 #2
BASE M/E: 256
RIC: 97664.
100.0
50.0
24224.
SULPHUR (S_8)
256
128
160
192
96
- S
- S
- S
- S_2
110
206
224
240
288
M/E
100
150
200
250

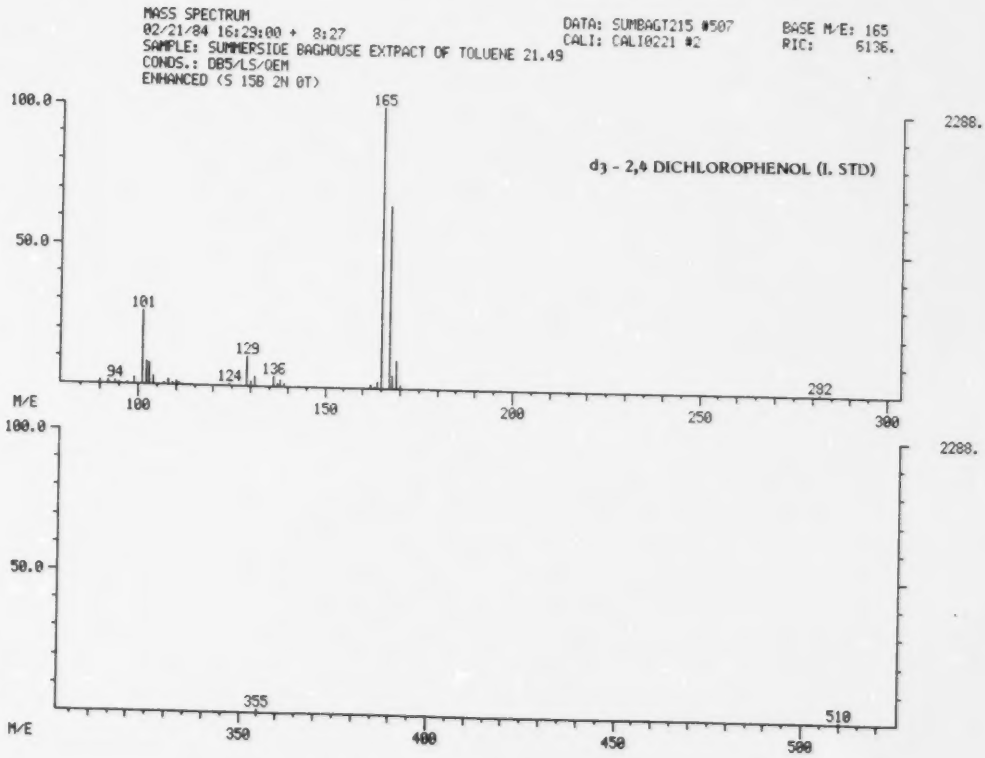

MASS SPECTRUM
02/21/84 17:09:00 + 22:14
SAMPLE: SUMMERSIDE BAGHOUSE BENZENE EXTRACT
CONDS.: DB5/LS/QEM
ENHANCED (S 15B 2N 0T)
DATA: SUMBAGB1 #1334
CALI: CALI0221 #2
BASE M/E: 202
RIC: 5568.
FLUORANTHENE
100.0
50.0
M/E
202
2380.
101
95
110
122
131
139
150
163
174
258
100
120
140
160
180
200
220
240
260

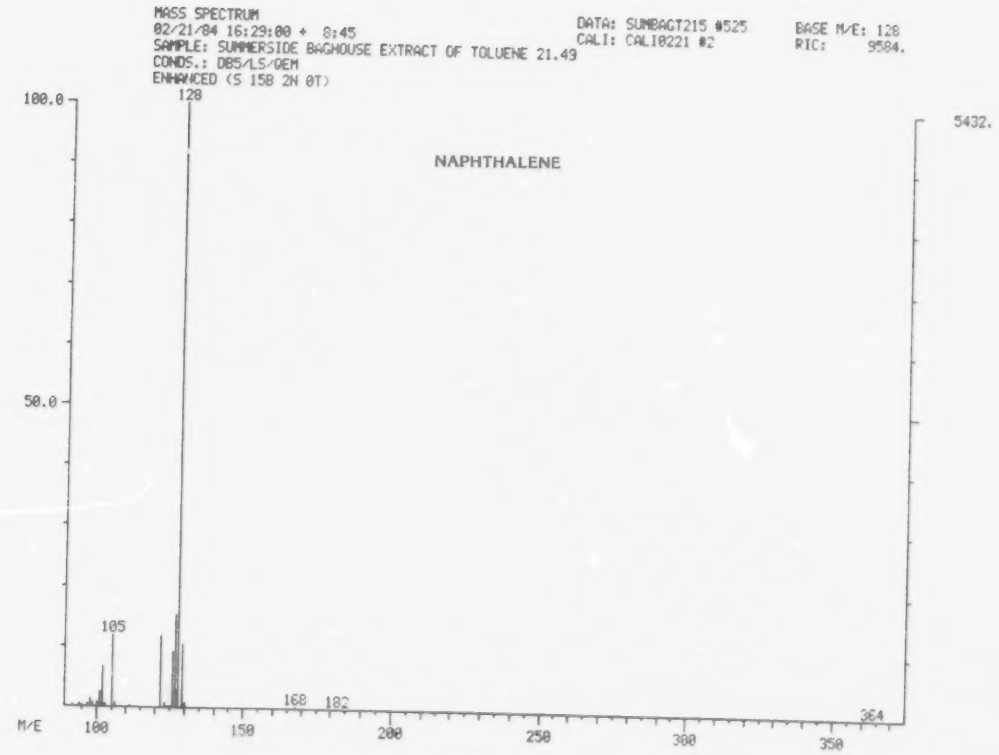

MASS SPECTRUM
02/21/84 17:09:00 + 26:35
SAMPLE: SUMMERSIDE BAGHOUSE BENZENE EXTRACT
CONDS.: DB5/LS/QEM
ENHANCED (S 15B 2N 0T)
DATA: SUMBAGB1 #1595
CALI: CALI0221 #2
BASE M/E: 149
RIC: 39424.
PHTHALATE IMPURITY
100.0
50.0
M/E
149
13392.
167
93
104
113
121
132
180
191
203
221
231
100
120
140
160
180
200
220
240
100.0
50.0
M/E
19392.
279
249
261
268
290
300
320
340
360
380
400

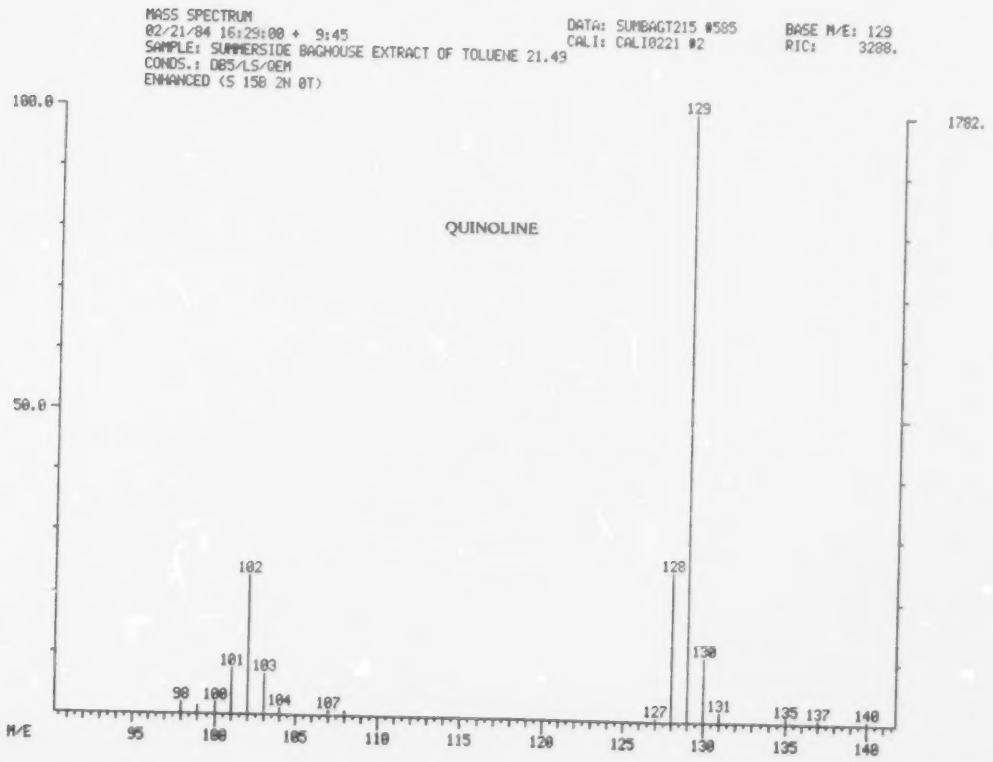

RIC
02/21/84 16:29:00
DATA: SUMBAGT215 #1
CALI: CALI0221 #2
SCANS 200 TO 2000
SAMPLE: SUMMERSIDE BAGHOUSE EXTRACT OF TOLUENE 21.49
CONDS.: DB5/LS/QEM
RANGE: G 1,2100 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3
100.0
212480.
RIC
1332
1111
874
1595
1504
270
408
460
525
585
738
958
1668
1769
1313
500
8:20
1000
16:40
1500
25:00
2000 SCAN
33:20 TIME

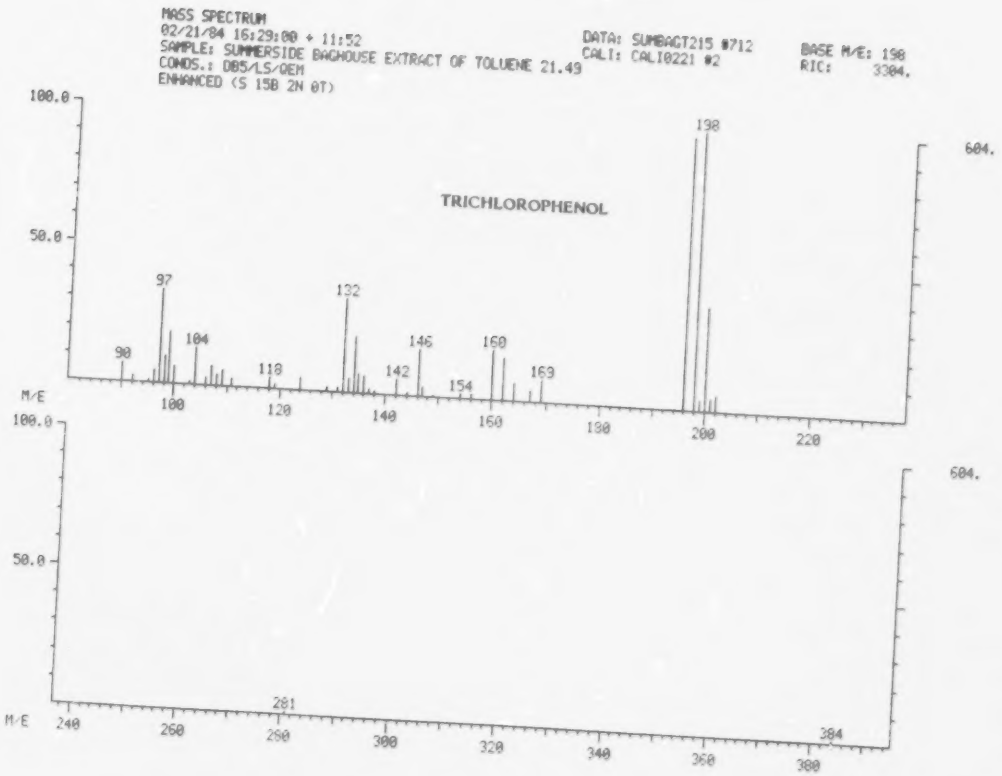

MASS SPECTRUM
02/21/84 16:29:00 + 4:30
DATA: SUMBAGT215 #270
CALI: CALI0221 #2
BASE M/E: 105
RIC: 15360.
SAMPLE: SUMMERSIDE BAGHOUSE EXTRACT OF TOLUENE 21.49
CONDS.: DB5/LS/QEM
ENHANCED (S 15B 2N 0T)
100.0
105
8000.
TOLUENE IMPURITY
50.0
90
122
231


MASS SPECTRUM
02/21/84 16:29:00 + 4:30
SAMPLE: SUMMERSIDE BAGHOUSE EXTRACT OF TOLUENE 21.49
CONDS.: DB5/LS/OEM
ENHANCED (S 15B 2N 0T)
DATA: SUMBAGT215 #270
CALI: CALI0221 #2
BASE M/E: 105
RIC: 15360.
100.0
50.0
105
8000.
TOLUENE IMPURITY
90
122
231
M/E
100
120
140
160
180
200
220


MASS SPECTRUM
02/21/84 16:29:00 + 8:27
SAMPLE: SUMMERSIDE BAGHOUSE EXTRACT OF TOLUENE 21.49
CONDS.: DB5/LS/OEM
ENHANCED (S 15B 2N 0T)
DATA: SUMBAGT215 #507
CALI: CALI0221 #2
BASE M/E: 165
RIC: 6136.
100.0
50.0
165
2288.
d3 - 2,4 DICHLOROPHENOL (I. STD)
101
129
94
124
136
292
M/E
100
150
200
250
300
100.0
50.0
2288.
355
510
M/E
350
400
450
500


MASS SPECTRUM
02/21/84 16:29:00 + 8:45
SAMPLE: SUMMERSIDE BAGHOUSE EXTRACT OF TOLUENE 21.43
CONDS.: DB5/LS/OEM
ENHANCED (S 15B 2N 0T)
DATA: SUMBAGT215 #525
CALI: CALI0221 #2
BASE M/E: 128
RIC: 9584.
NAPHTHALENE
100.0
50.0
128
5432.
105
168
182
364
M/E
100
150
200
250
300
350


MASS SPECTRUM
02/21/84 16:29:00 + 9:45
SAMPLE: SUMMERSIDE BAGHOUSE EXTRACT OF TOLUENE 21.43
CONDS.: DB5/LS/OEM
ENHANCED (S 15B 2N 0T)
DATA: SUMBAGT215 #585
CALI: CALI0221 #2
BASE M/E: 129
RIC: 3288.
QUINOLINE
100.0
50.0
129
1782.
102
128
101
103
130
98
100
104
107
127
131
135
137
140
M/E
95
100
105
110
115
120
125
130
135
140


MASS SPECTRUM
02/21/84 16:29:00 + 11:52
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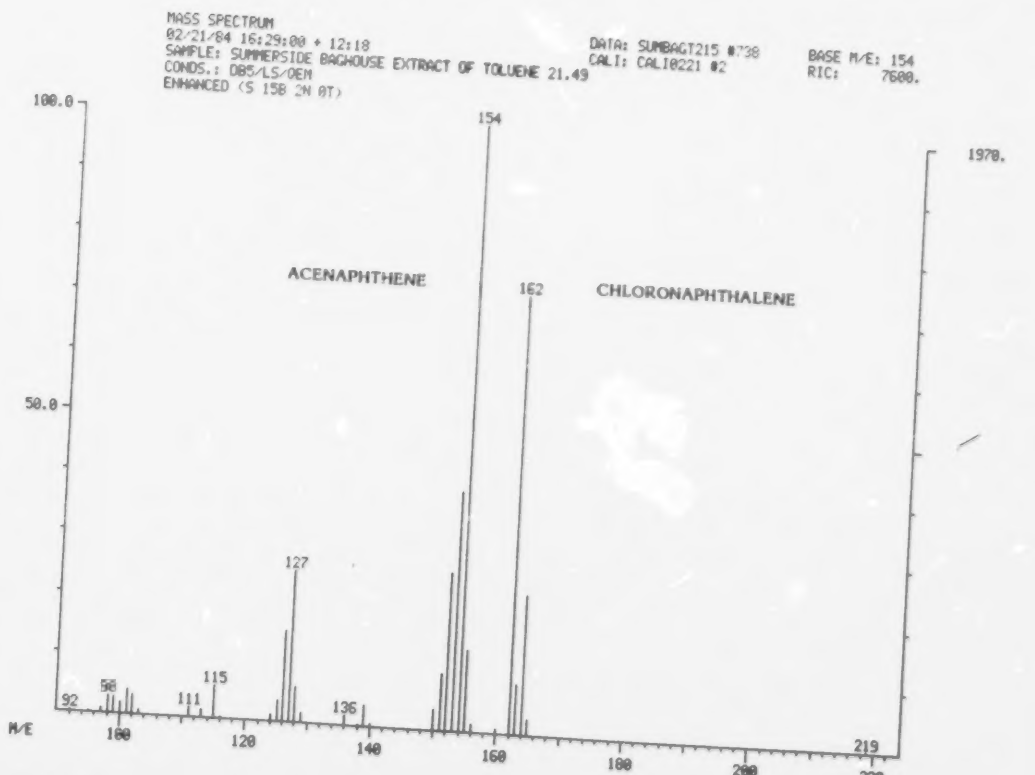
CONDS.: DB5/LS/OEM
ENHANCED (S 15B 2N 0T)
DATA: SUMBAGT215 #712
CALI: CALI0221 #2
BASE M/E: 198
RIC: 3304.
TRICHLOROPHENOL
604.
604.
M/E


MASS SPECTRUM
02/21/84 16:29:00 + 12:18
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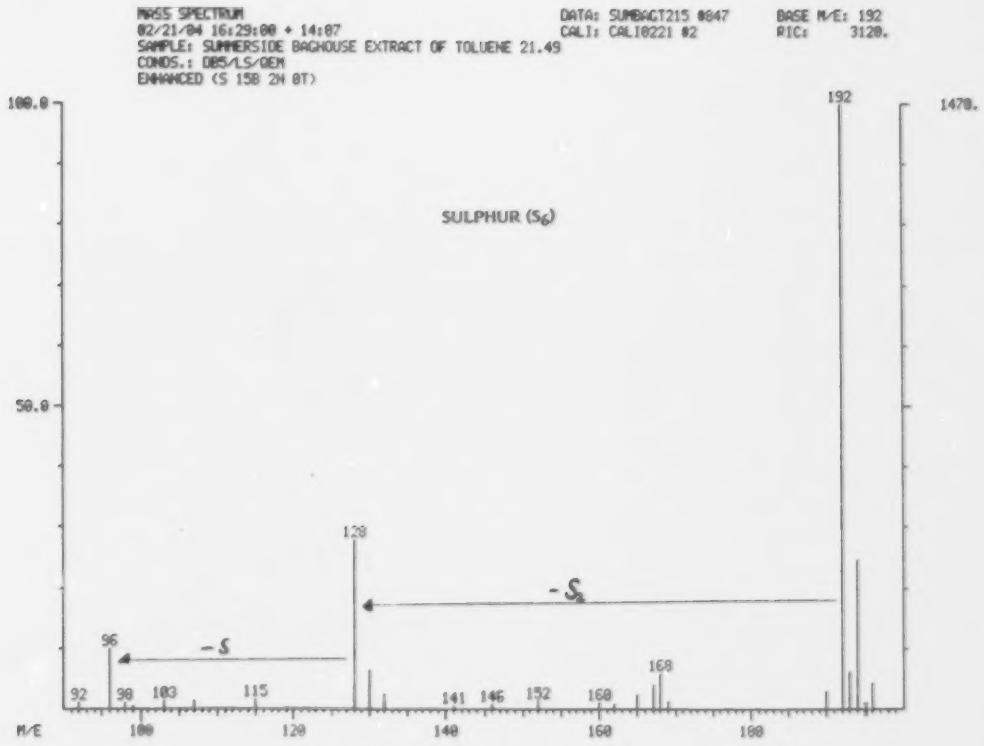
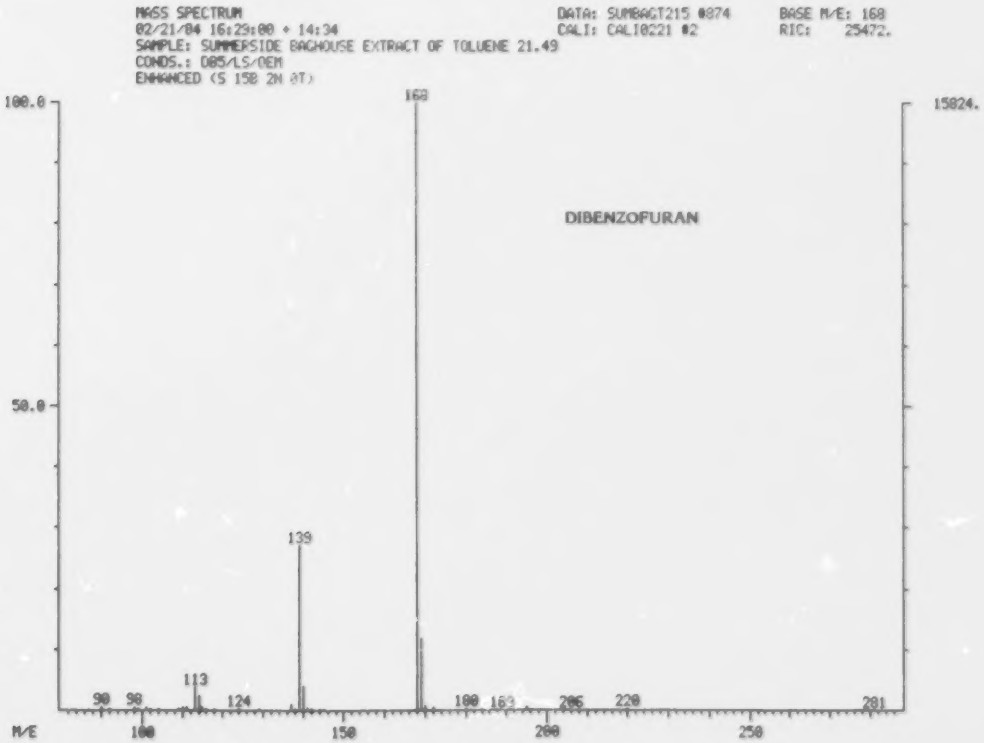
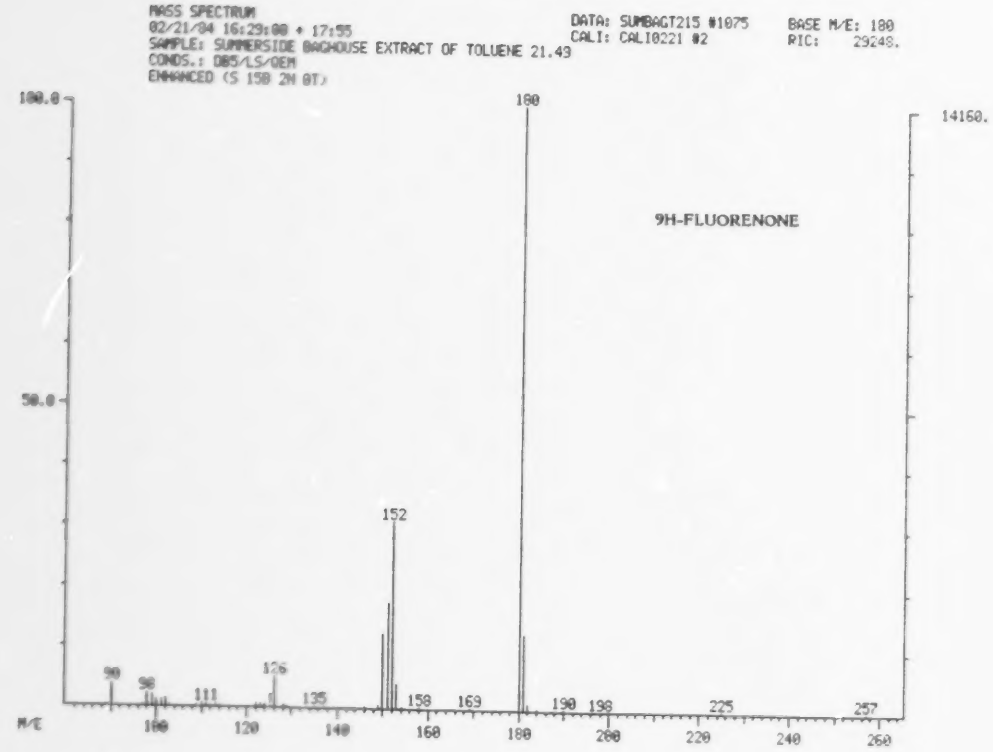
CONDS.: DB5/LS/OEM
ENHANCED (S 15B 2N 0T)
DATA: SUMBAGT215 #738
CALI: CALI0221 #2
BASE M/E: 154
RIC: 7600.
ACENAPHTHENE
CHLORONAPHTHALENE
1970.
M/E


MASS SPECTRUM
02/21/84 16:29:00 • 14:07
SAMPLE: SUMMERSIDE BAGHOUSE EXTRACT OF TOLUENE 21.49
CONDS.: DB5/LS/OEM
ENHANCED (S 150 2N 0T)
DATA: SUMBAGT215 0047
CALI: CALI0221 #2
BASE M/E: 192
RIC: 3120.
100.0
50.0
1470.
192
SULPHUR (S_6)
128
- S_2
96
- S
168
92
98
103
115
141
146
152
160
M/E
100
120
140
160
180


MASS SPECTRUM
02/21/84 16:29:00 • 14:34
SAMPLE: SUMMERSIDE BAGHOUSE EXTRACT OF TOLUENE 21.49
CONDS.: DB5/LS/OEM
ENHANCED (S 150 2N 0T)
DATA: SUMBAGT215 0074
CALI: CALI0221 #2
BASE M/E: 168
RIC: 25472.
100.0
50.0
15824.
168
DIBENZOFURAN
139
113
90
98
124
180
183
205
220
281
M/E
100
150
200
250


MASS SPECTRUM
02/21/84 16:29:00 + 17:55
SAMPLE: SUMMERSIDE BAGHOUSE EXTRACT OF TOLUENE 21.49
CONDS.: DB5/LS/QEM
ENHANCED (S 150 2N 0T)
DATA: SUMBAGT215 #1075
CALI: CALI0221 #2
BASE M/E: 180
RIC: 29248.
100.0
50.0
14160.
180
152
9H-FLUORENONE
90
98
111
126
135
158
169
190
198
225
257
M/E
100
120
140
160
180
200
220
240
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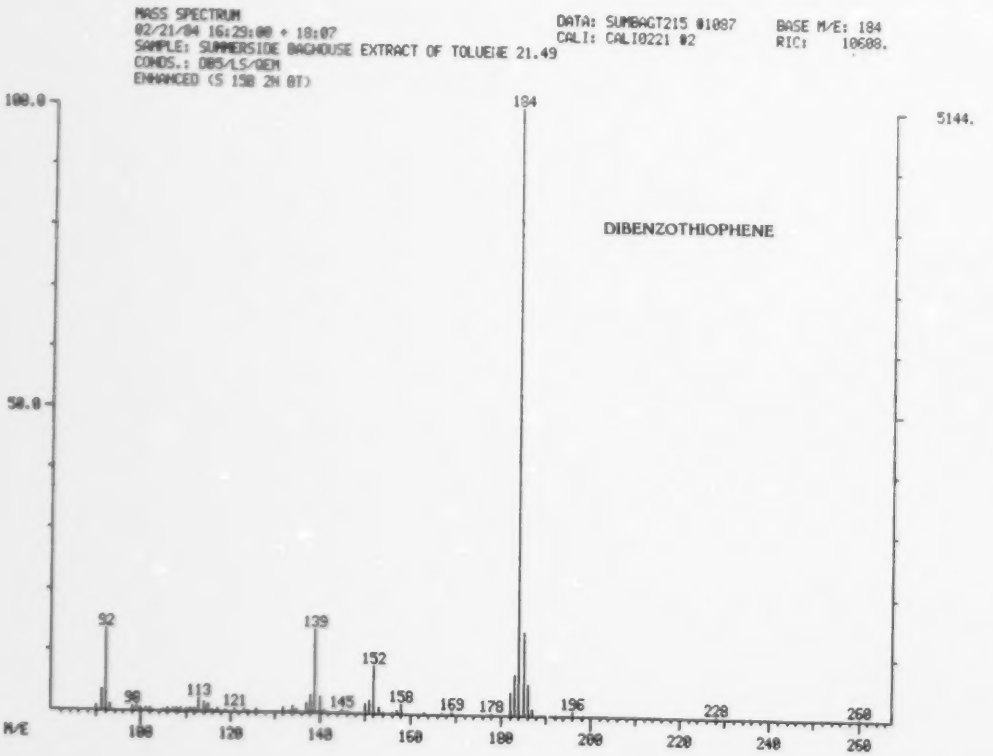
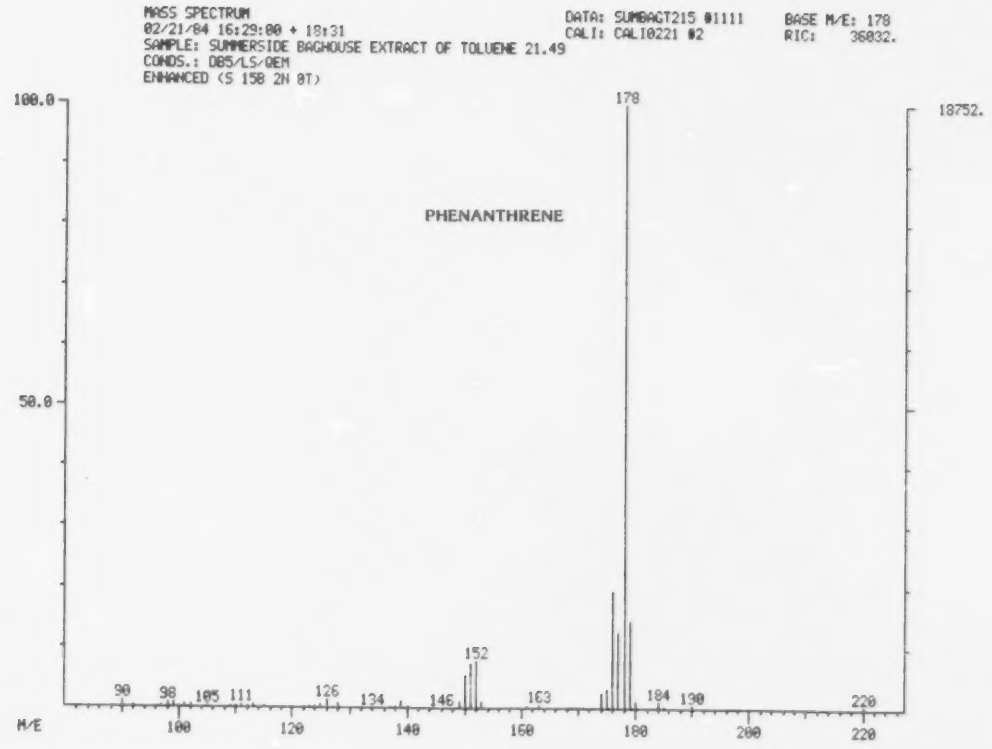
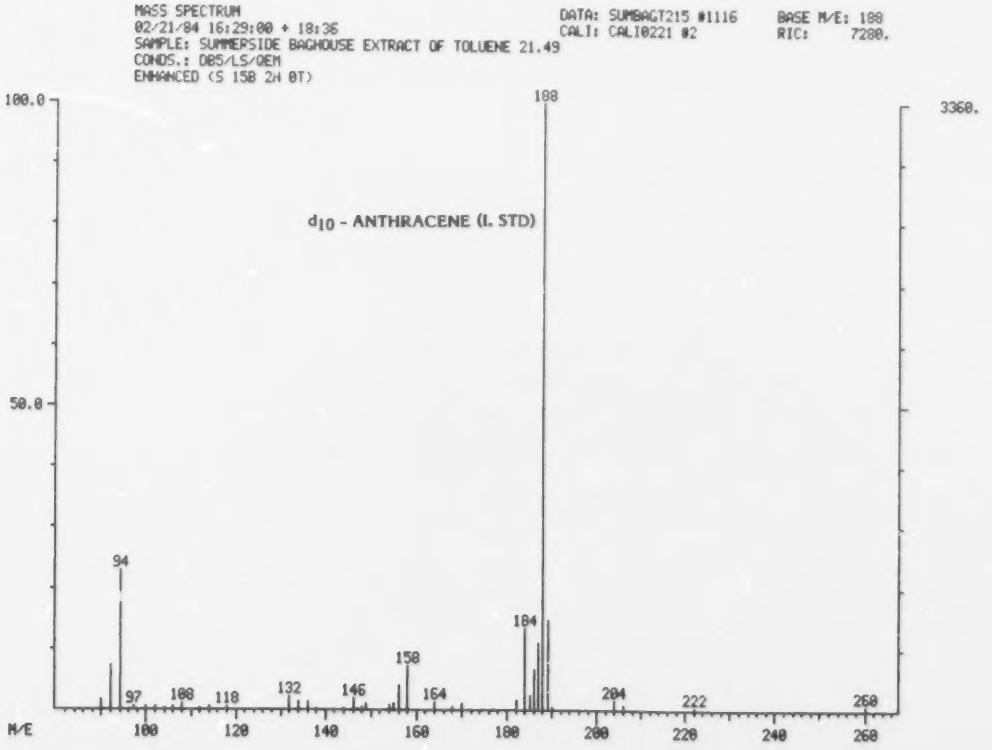
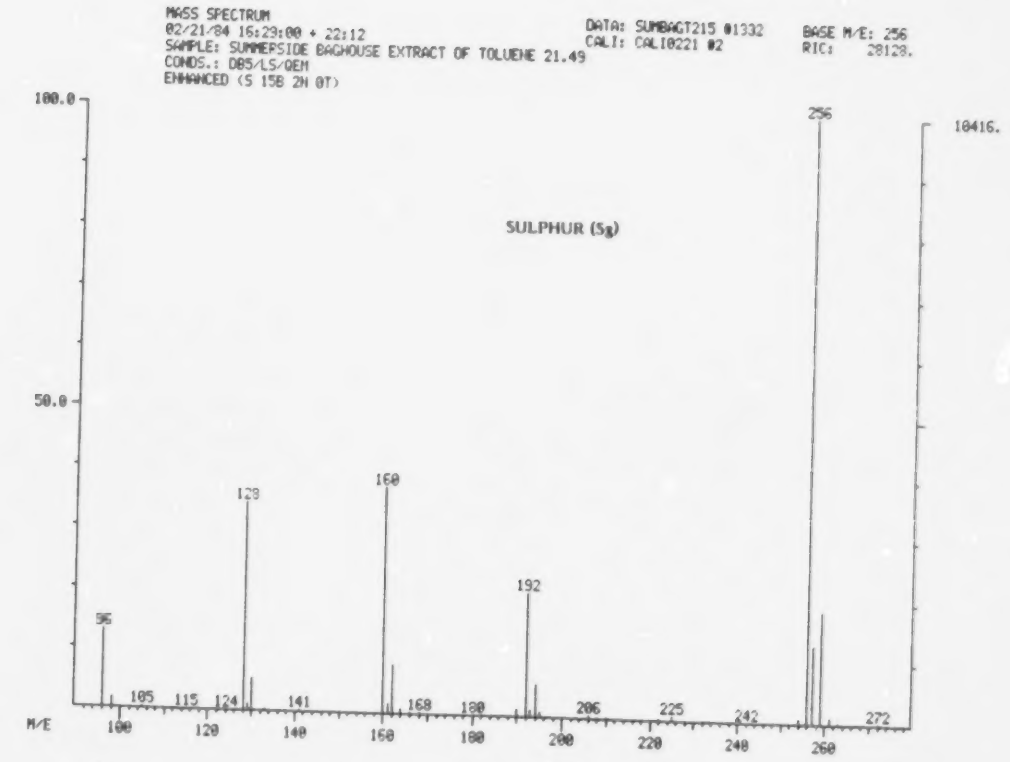
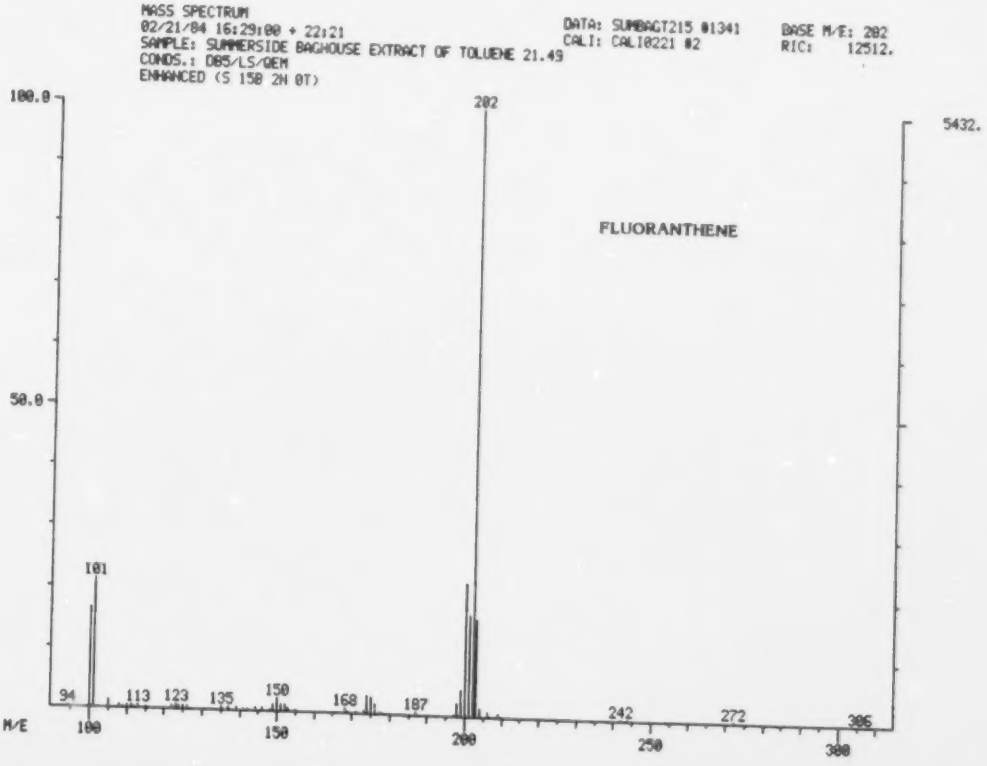
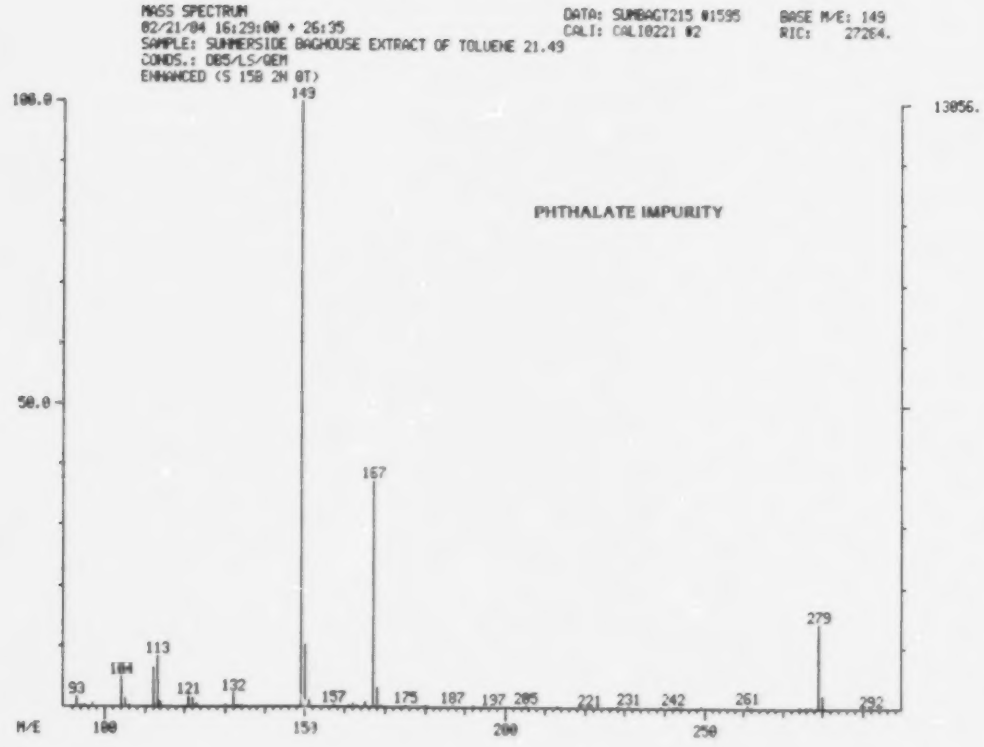

MASS SPECTRUM
02/21/84 16:29:00 + 18:07
SAMPLE: SUMMERSIDE BAGHOUSE EXTRACT OF TOLUEIE 21.49
CONDS.: DB5/LS/QEM
ENHANCED (S 150 2N 0T)
DATA: SUMBAGT215 #1087
CALI: CALI0221 #2
BASE M/E: 184
RIC: 10608.
100.0
50.0
5144.
184
DIBENZOTHIOPHENE
92
139
152
98
113
121
145
158
169
178
196
228
260
M/E
100
120
140
160
180
200
220
240
260

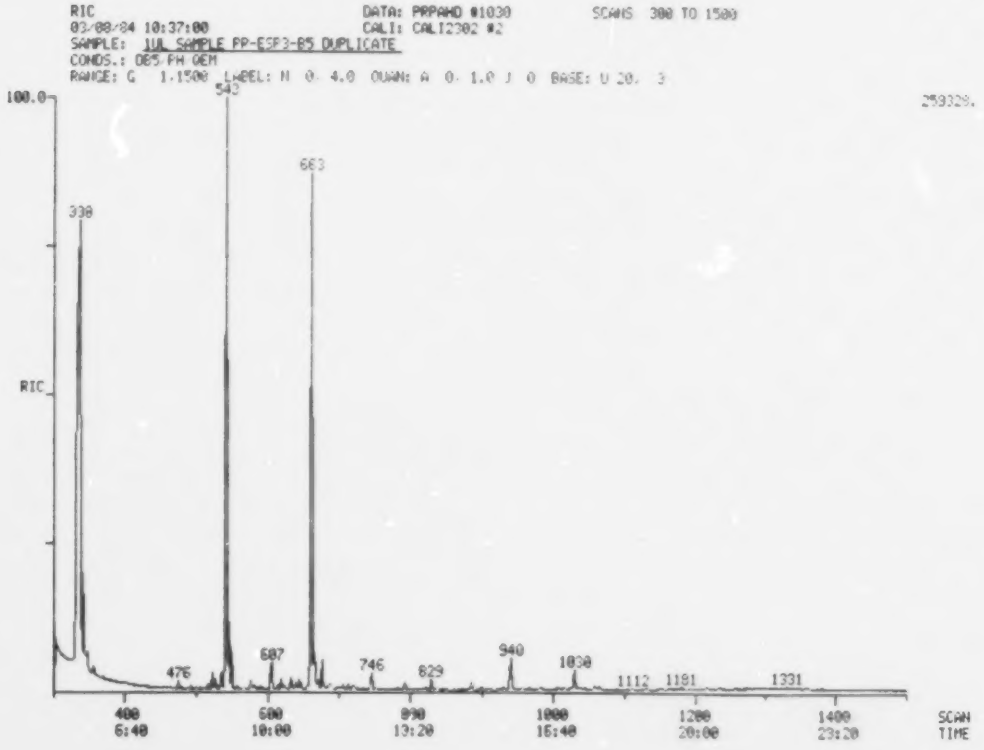

MASS SPECTRUM
02/21/84 16:29:00 + 18:31
SAMPLE: SUMMERSIDE BAGHOUSE EXTRACT OF TOLUENE 21.49
CONDS.: DB5/LS/QEM
ENHANCED (S 15B 2N 0T)
DATA: SUMBAGT215 #1111
CALI: CALI0221 #2
BASE M/E: 178
RIC: 36032.
100.0
50.0
178
18752.
PHENANTHRENE
152
90 98 105 111 126 134 146 163 184 190 220
M/E
100 120 140 160 180 200 220


MASS SPECTRUM
02/21/84 16:29:00 + 18:36
SAMPLE: SUMMERSIDE BAGHOUSE EXTRACT OF TOLUENE 21.49
CONDS.: DB5/LS/QEM
ENHANCED (S 15B 2N 0T)
DATA: SUMBAGT215 #1116
CALI: CALI0221 #2
BASE M/E: 188
RIC: 7280.
100.0
50.0
188
3360.
d10 - ANTHRACENE (I. STD)
94
184
158
97 108 118 132 146 164 204 222 260
M/E
100 120 140 160 180 200 220 240 260


MASS SPECTRUM
02/21/84 16:29:00 + 22:12
SAMPLE: SUMMERSIDE BAGHOUSE EXTRACT OF TOLUENE 21.49
CONDS.: DB5/LS/QEM
ENHANCED (S 15B 2N 0T)
DATA: SUMBAGT215 01332
CALI: CALI0221 #2
BASE M/E: 256
RIC: 28128.
100.0
50.0
M/E
SULPHUR (Sg)
256
10416.
128
160
192
96
105
115
124
141
168
180
206
225
242
272
100
120
140
160
180
200
220
240
260


MASS SPECTRUM
02/21/84 16:29:00 + 22:21
SAMPLE: SUMMERSIDE BAGHOUSE EXTRACT OF TOLUENE 21.49
CONDS.: DB5/LS/QEM
ENHANCED (S 15B 2N 0T)
DATA: SUMBAGT215 01341
CALI: CALI0221 #2
BASE M/E: 202
RIC: 12512.
100.0
50.0
M/E
FLUORANTHENE
202
5432.
101
94
113
123
135
150
168
187
242
272
306
100
150
200
250
300

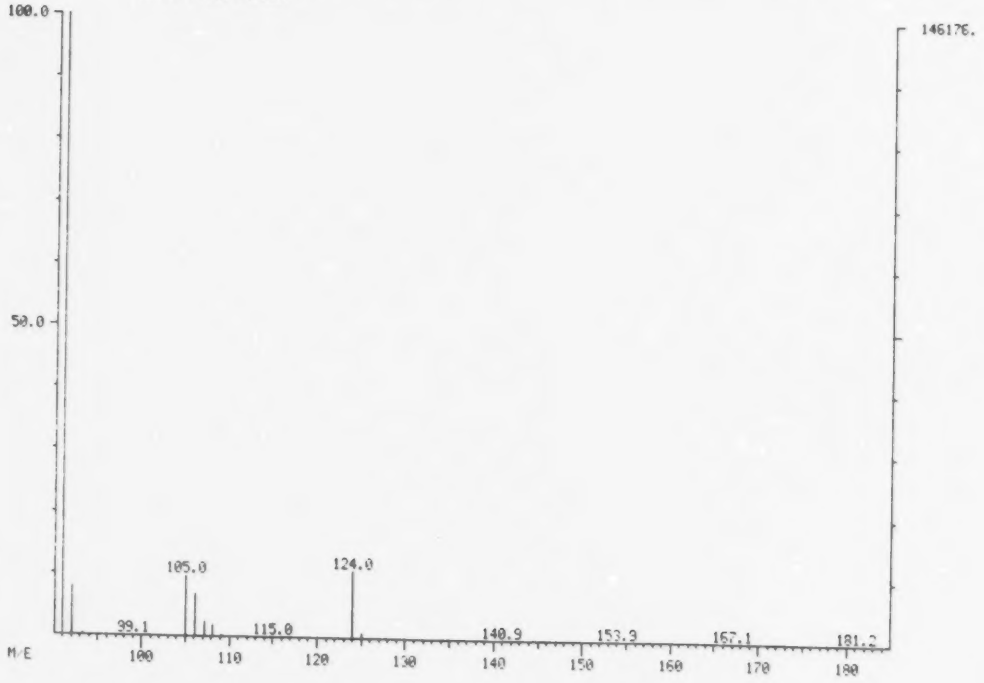

MASS SPECTRUM
02/21/04 16:29:00 + 26:35
SAMPLE: SUMMERSIDE BAGHOUSE EXTRACT OF TOLUENE 21.49
CONDS.: DB5/LS/QEM
ENHANCED (S 15B 2N 0T)
DATA: SUMBAGT215 #1595
CALI: CALI0221 #2
BASE M/E: 149
RIC: 27264.
100.0
50.0
149
167
279
113
104
93
121
132
157
175
187
197
205
221
231
242
261
292
M/E
100
150
200
250
13056.
PHTHALATE IMPURITY


RIC
03/08/04 10:37:00
SAMPLE: 1UL SAMPLE PP-ESF3-B5 DUPLICATE
CONDS.: DB5 FH QEM
RANGE: G 1:1500 LABEL: N 0. 4.0 QUAN: A 0. 1.0 J 0 BASE: U 20. 3
DATA: PRPAMD #1030
SCANS 300 TO 1500
259328.
100.0
RIC
543
683
308
476
687
746
829
940
1030
1112
1181
1331
400
6:40
600
10:00
800
13:20
1000
16:40
1200
20:00
1400
23:20
SCAN
TIME

MASS SPECTRUM
03/08/84 10:37:00 + 5:38
SAMPLE: 1UL SAMPLE PR-ESP3-B5 DUPLICATE
CONDS.: DB5/PH/OEM

DATA: PRPAHD #338
CALI: CALI2302 #2

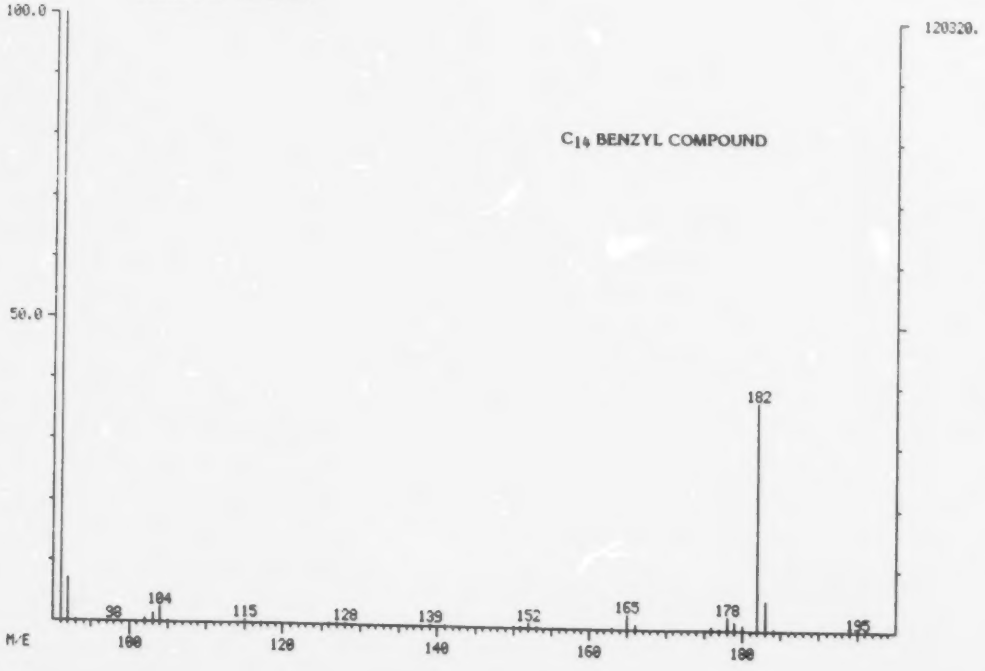
BASE M/E: 91
RIC: 205312.



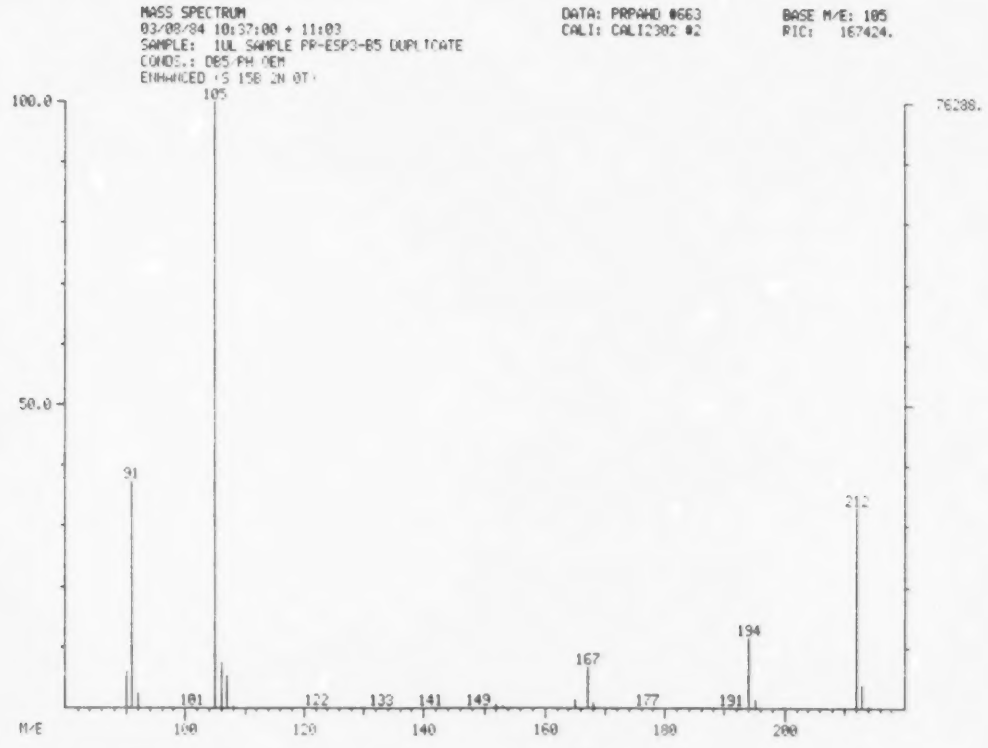
MASS SPECTRUM
03/08/84 10:37:00 + 9:03
SAMPLE: 1UL SAMPLE PR-ESP3-B5 DUPLICATE
CONDS.: DB5/PH/OEM
ENHANCED (S 15B 2N 0T)

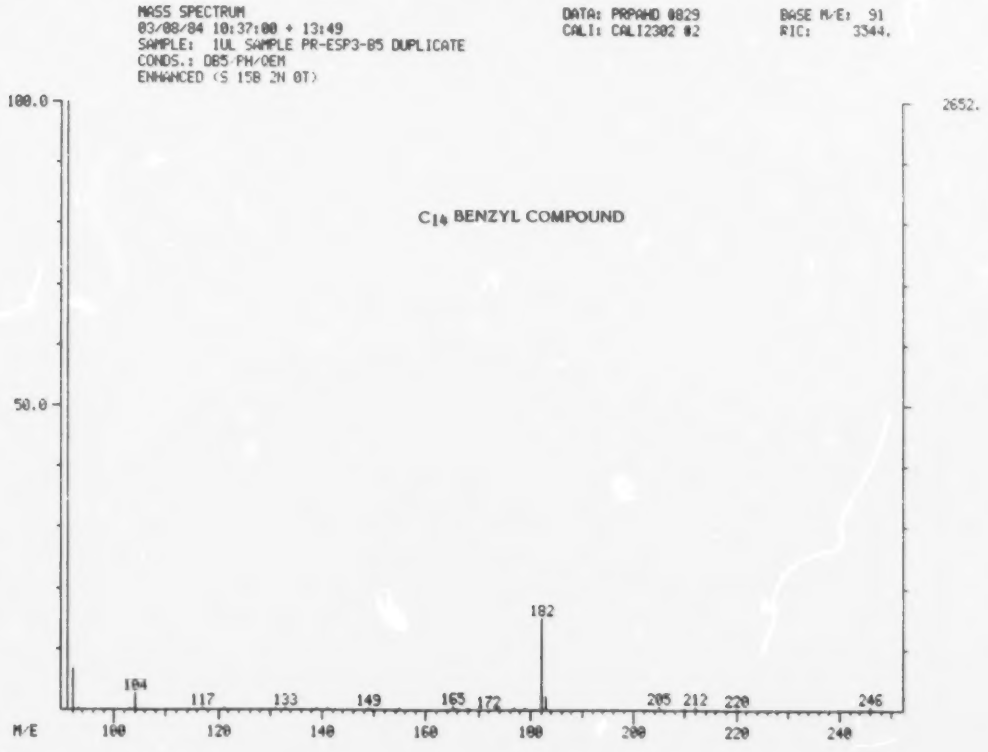
DATA: PRPAHD #543
CALI: CALI2302 #2

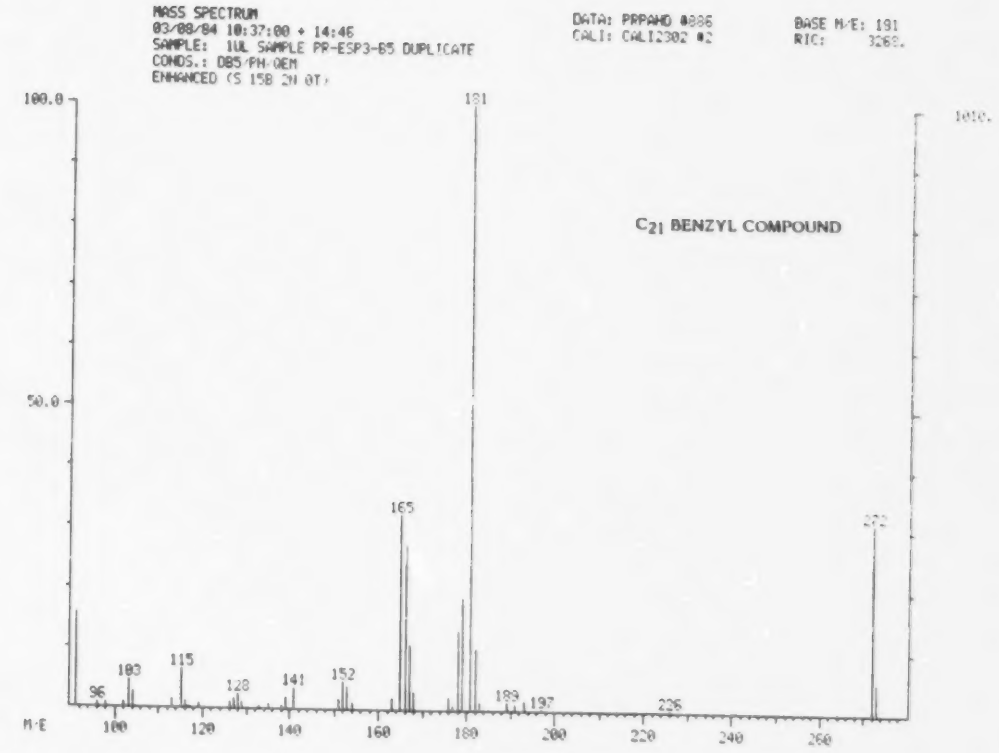
BASE M/E: 91
RIC: 200192.



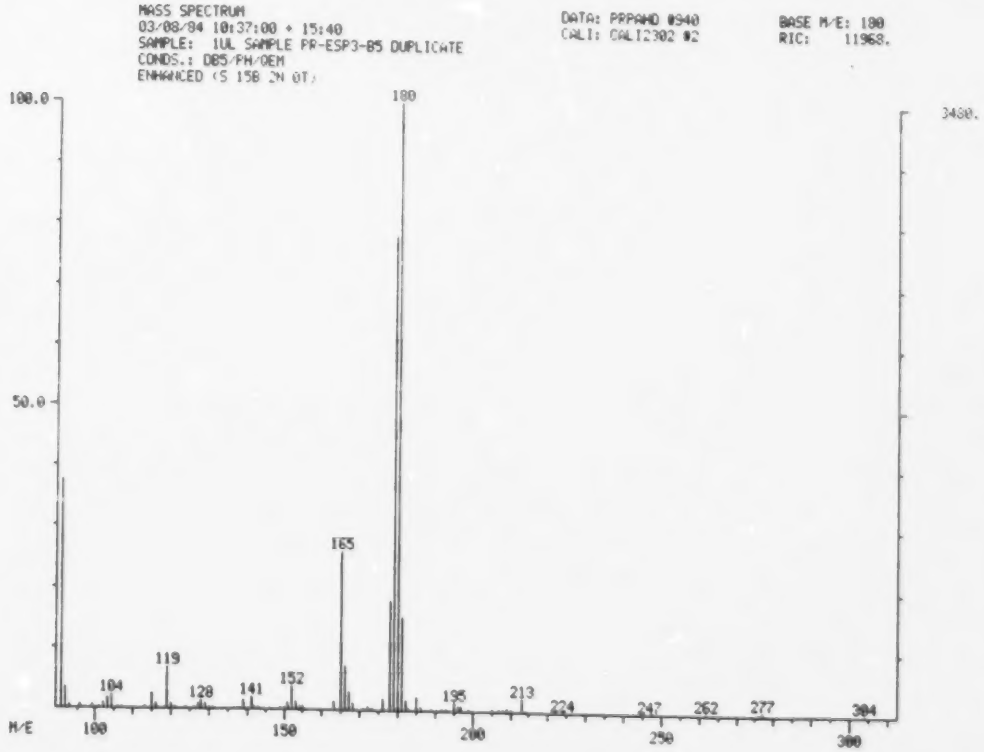
C_{14} BENZYL COMPOUND


MASS SPECTRUM
03/08/84 10:37:00 + 11:03
SAMPLE: 1UL SAMPLE PR-ESP3-B5 DUPLICATE
CONDS.: DB5/PH/OEM
ENHANCED (S 15B 2N 0T)
DATA: PRPAHD 0663
CALI: CALI2302 02
BASE M/E: 105
RIC: 167424.
100.0
50.0
M/E
105
91
212
194
167
181
122
133
141
149
177
191
78208.
100
120
140
160
180
200


MASS SPECTRUM
03/08/84 10:37:00 + 13:49
SAMPLE: 1UL SAMPLE PR-ESP3-B5 DUPLICATE
CONDS.: DB5/PH/OEM
ENHANCED (S 15B 2N 0T)
DATA: PRPAHD 0829
CALI: CALI2302 02
BASE M/E: 91
RIC: 3544.
100.0
50.0
M/E
C14 BENZYL COMPOUND
182
104
117
133
149
163
172
205
212
220
246
2652.
100
120
140
160
180
200
220
240



C_{21} BENZYL COMPOUND



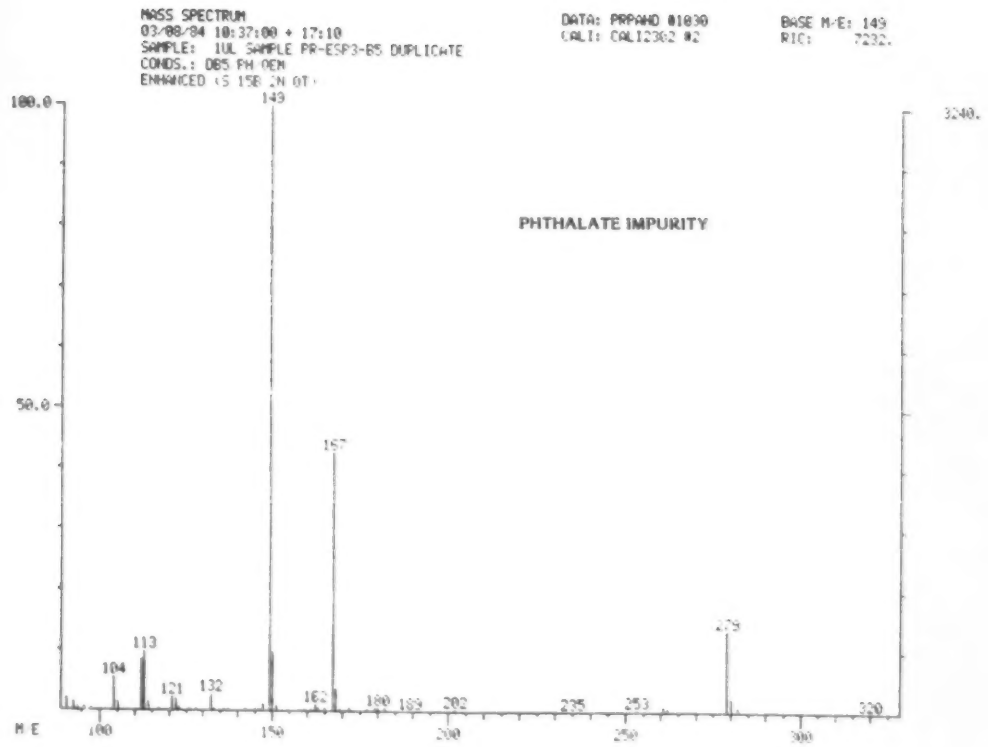


FIGURE A-1 $^{13}C_{12}$ PeCDD STANDARD

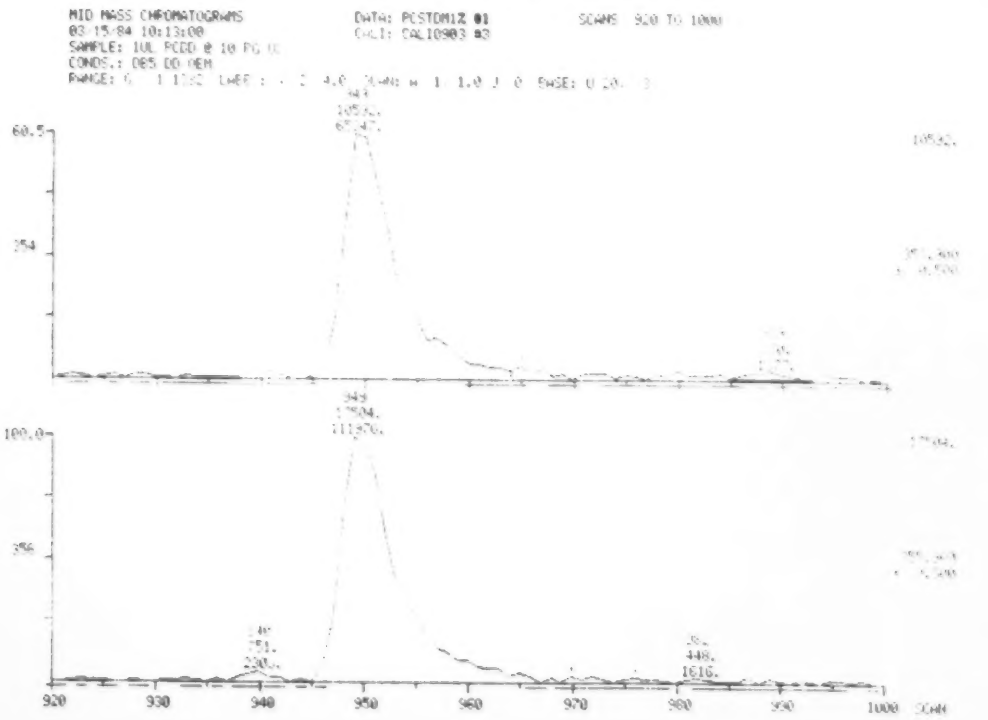


FIGURE A-2 3pg H_6CDF STD

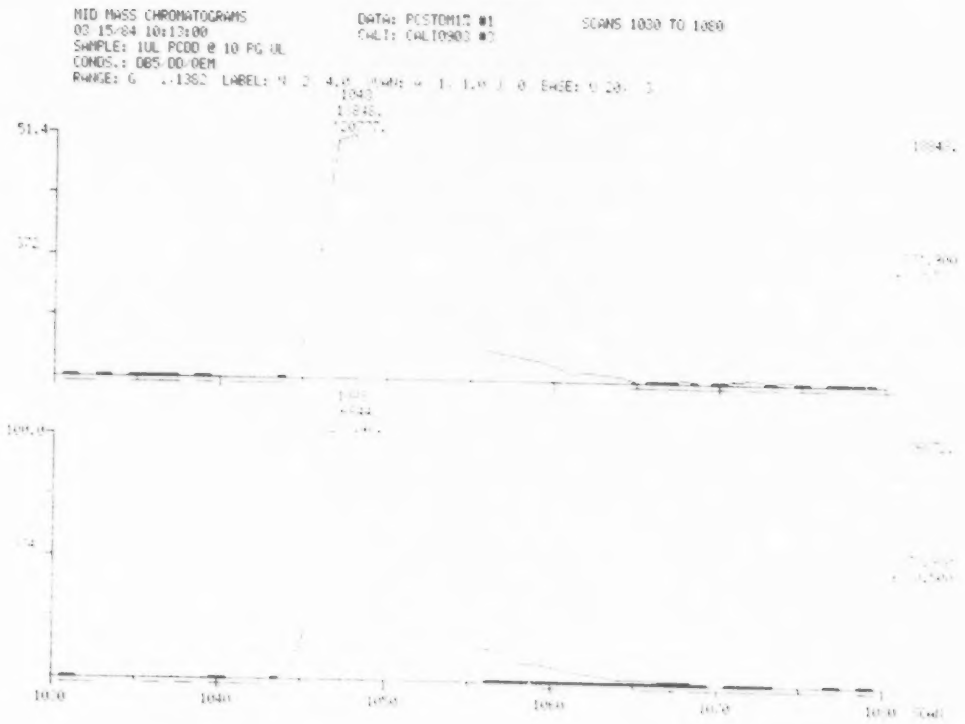


FIGURE A-3 10pg H_6CDD STANDARD

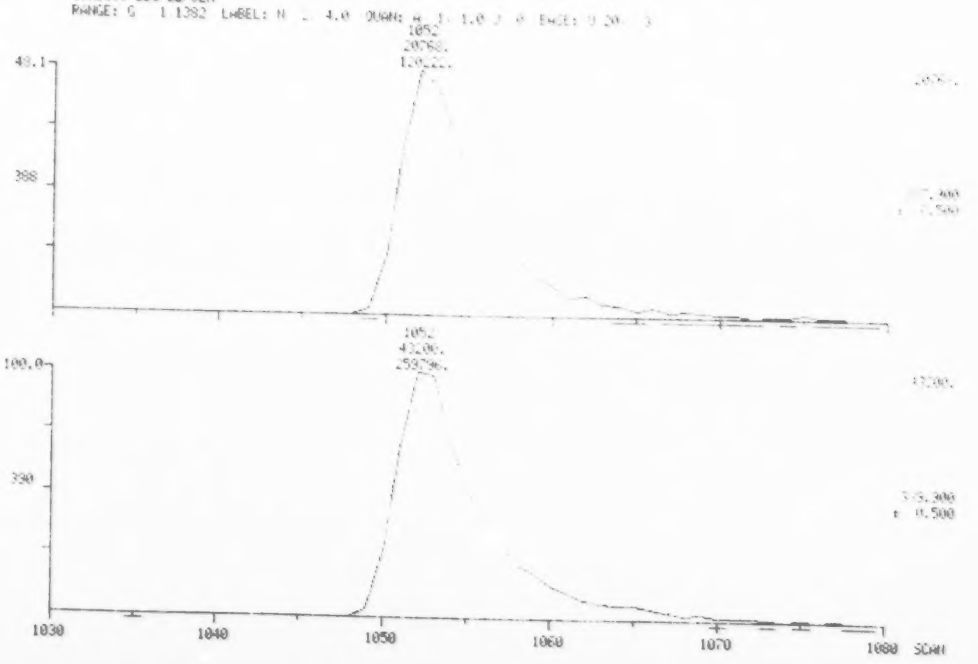


FIGURE A-4 10pg H_7CDD STANDARD

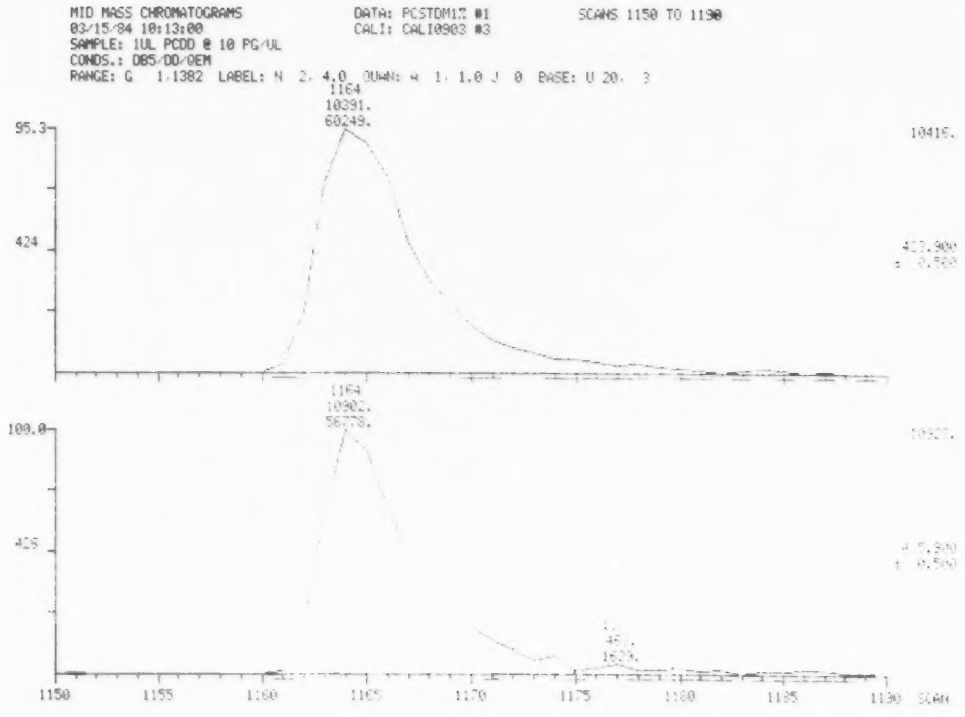


FIGURE A-5 10pg OCDD STANDARD

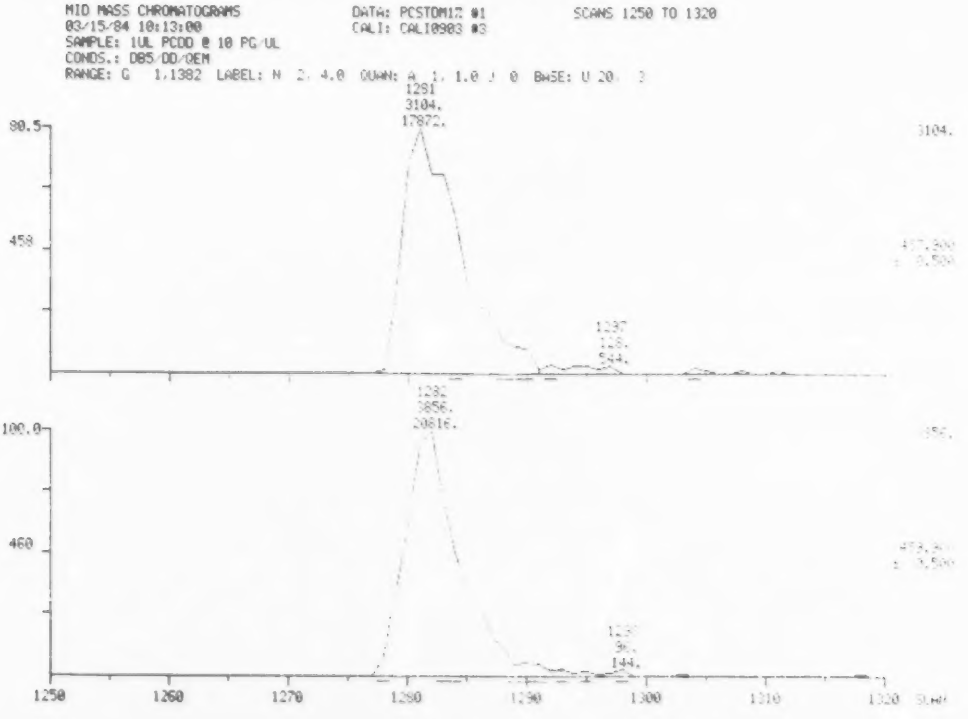


FIGURE A-6 10pg OCDF STANDARD

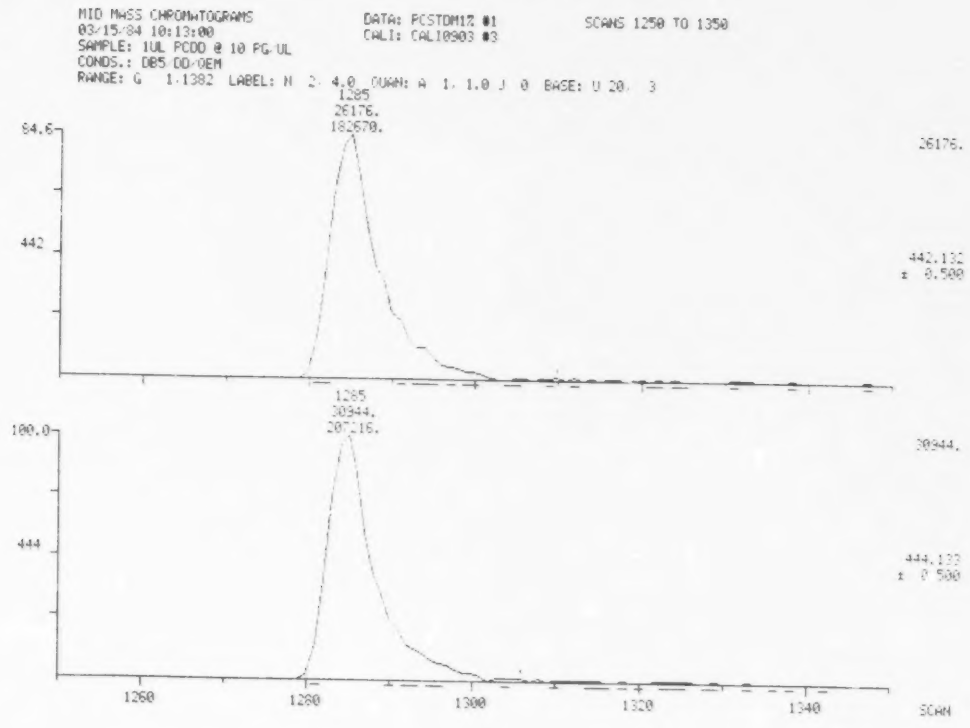


FIGURE A-6 10pg OCDF STANDARD

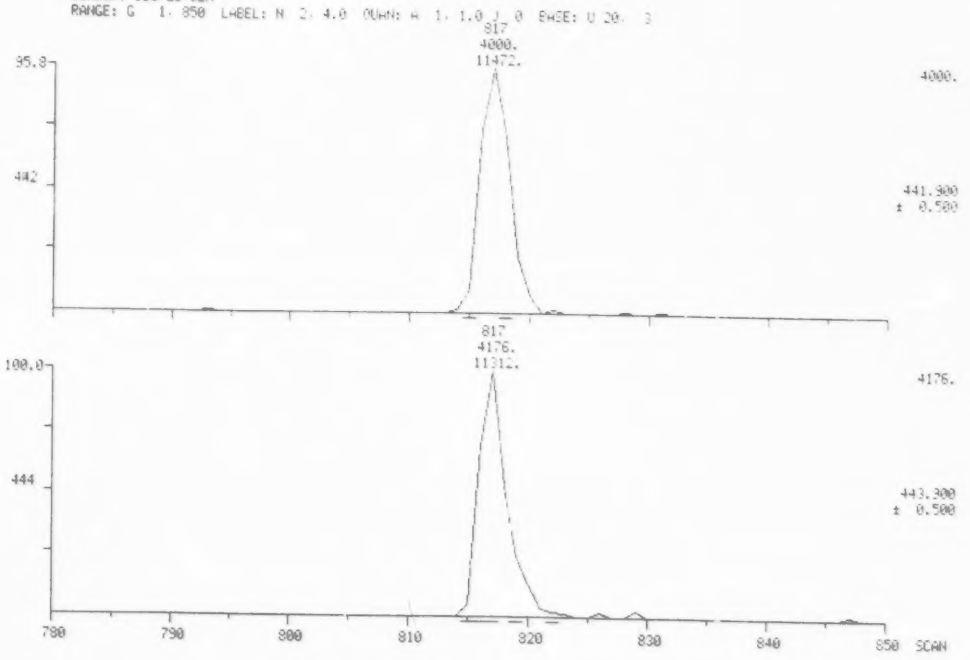


FIGURE A-7 P_5CDD/P_5CDF IN URBAN DUST

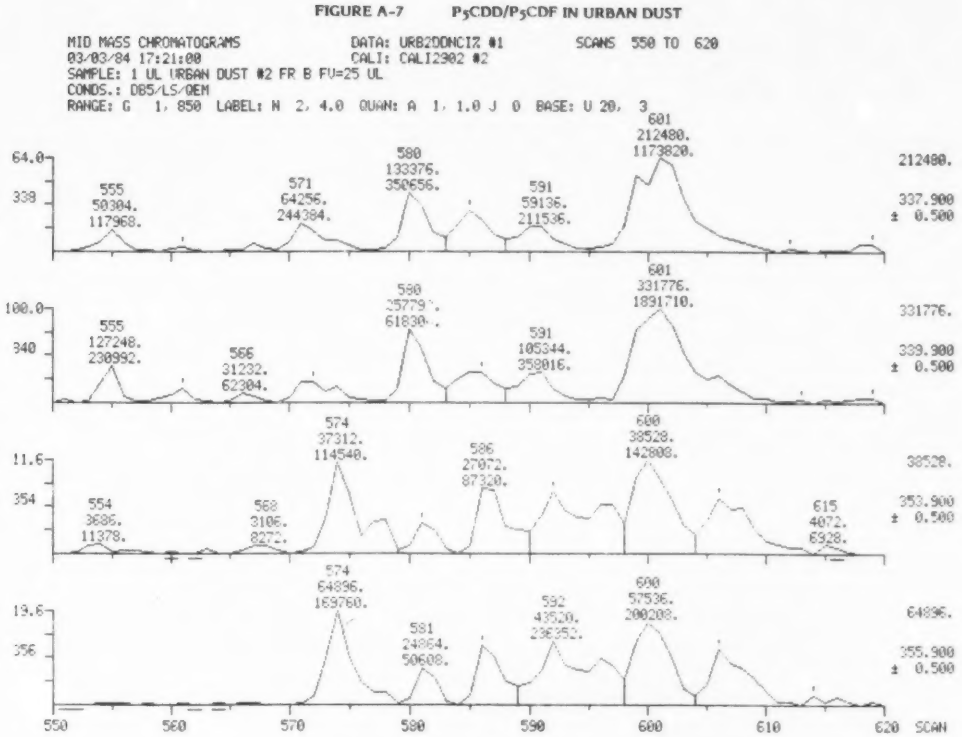


FIGURE A-8 H_6CDD/H_6CDF IN URBAN DUST

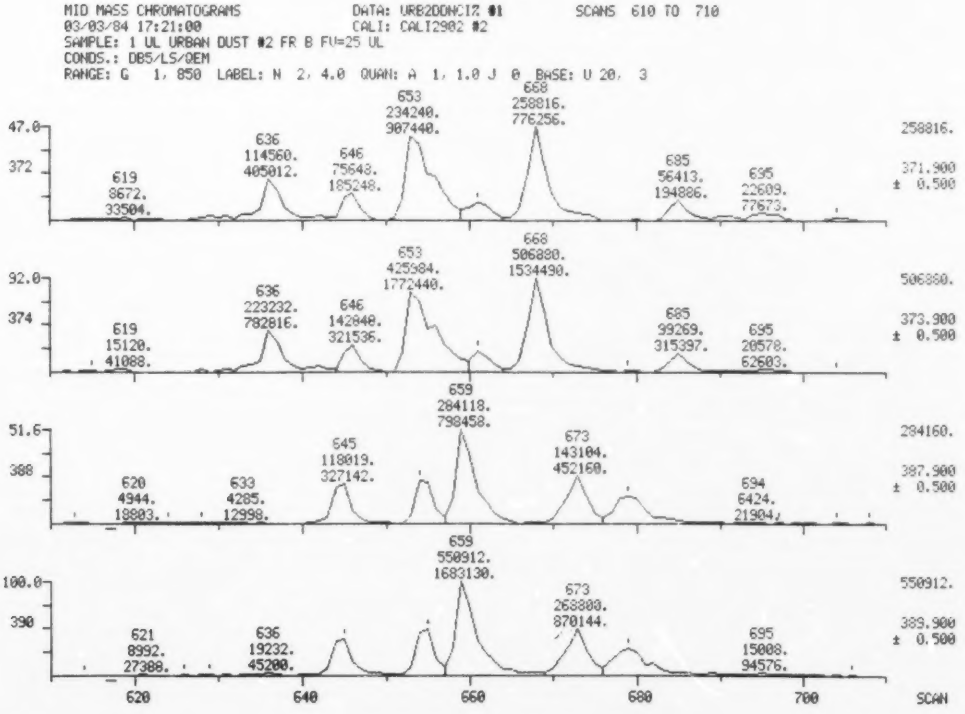


FIGURE A-9 H_7CDD/H_7CDF IN URBAN DUST

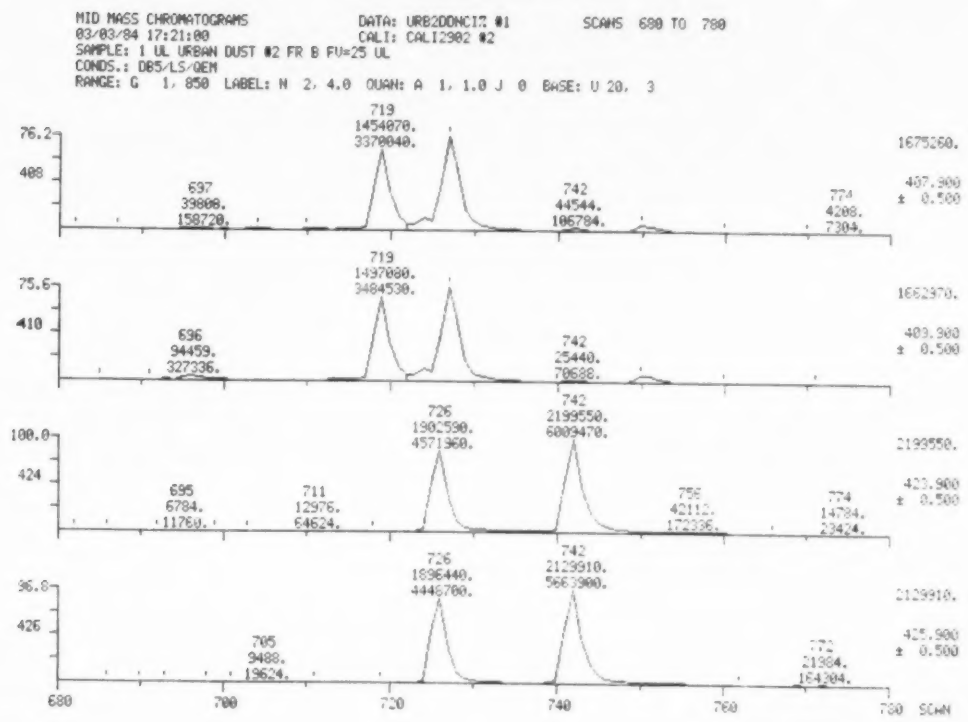


FIGURE A-10 OCDD IN URBAN DUST

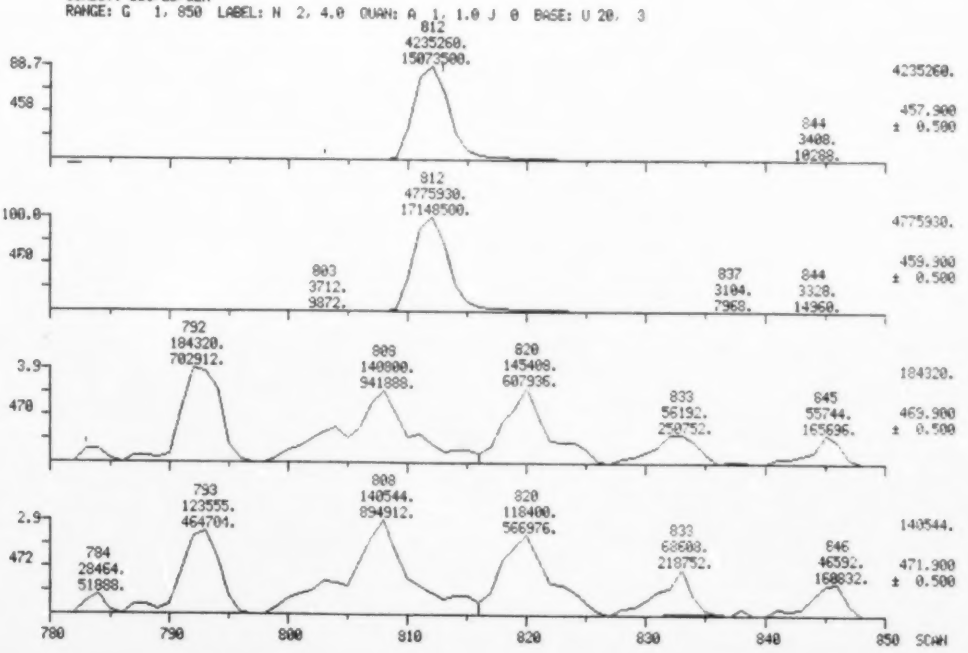
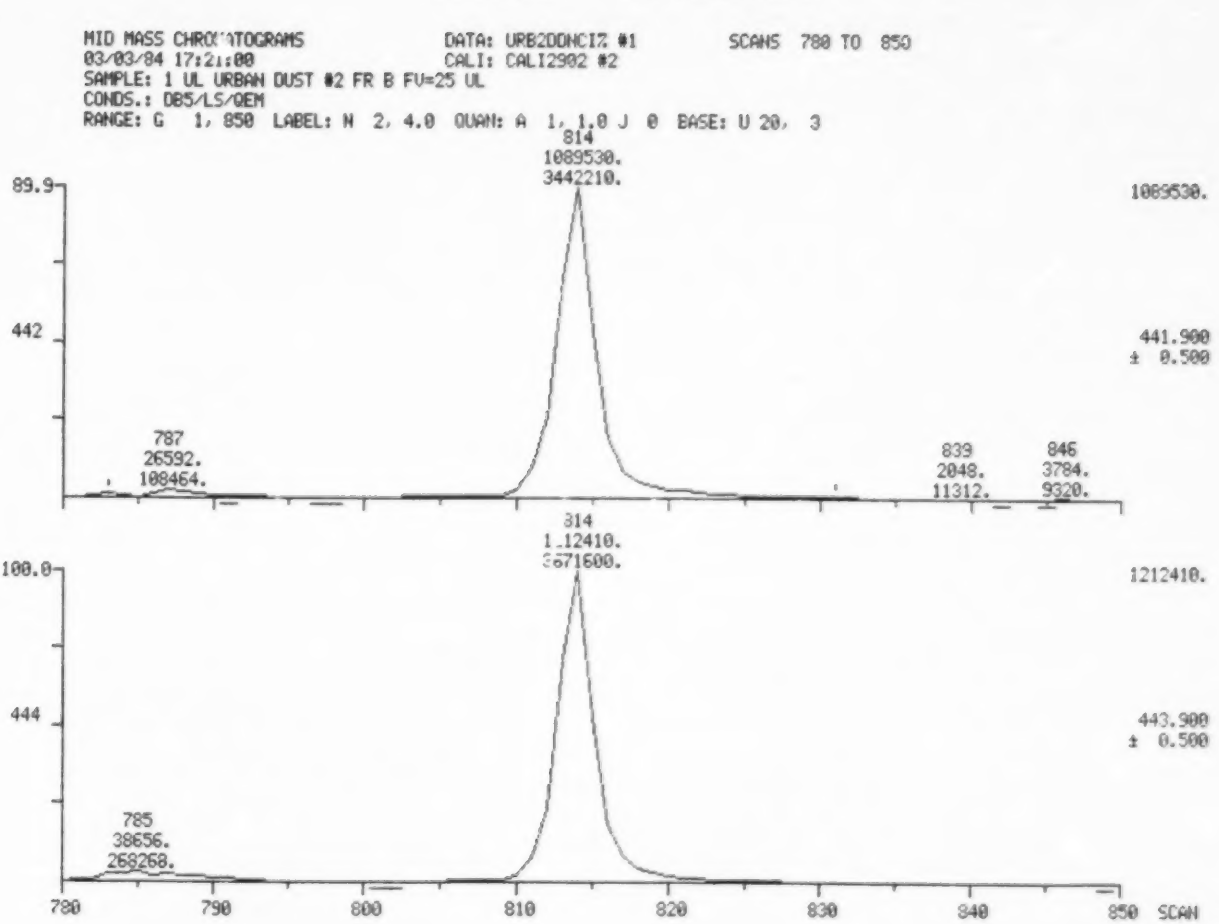


FIGURE A-11 OCDF IN URBAN DUST



APPENDIX B

GLOSSARY OF ABBREVIATIONS

PAH	polyaromatic hydrocarbon
ESP	electrostatic precipitator
AFBC	atmospheric fluidized-bed combustion
PCF	pulverized coal-fuelled
TEOX	total extractable organic chlorine
PCDD	polychlorinated dibenzo-p-dioxins
PCDF	polychlorinated dibenzofurans
RDF	refuse-derived fuel
GC	gas chromatography
MS	mass spectroscopy
HPLC	high-performance liquid chromatography
EI/MID	electron-impact/multiple-ion detection
NCI	negation-ion chemical ionization
UV	ultraviolet
HRGC	high-resolution gas chromatography
NBS	National Bureau of Standards (U.S.A.)